Geochemistry and Origin of Some Natural Gases in the Plateau Province, Central Appalachian Basin, Pennsylvania and Ohio¹

C. D. Laughrey² and F. J. Baldassare³

ABSTRACT

We sampled gases from 22 wells and 5 cores in western Pennsylvania and eastern Ohio to evaluate the possible use of stable isotope geochemistry for interpreting the origins of natural gases in the Plateau province of the central Appalachians and for correlating these gases with their probable sources. The isotope data suggest that several of these gases have multiple sources or were altered by geological or biogeochemical processes.

Gases produced from Upper Cambrian Rose Run sandstones in Portage County, Ohio, are condensate-associated hydrocarbons. These gases can be correlated to local Ordovician source rocks. Gases produced from the Upper Cambrian Beekmantown Dolomite in Coshocton County, Ohio, also are thermogenic, but the maturity of these hydrocarbons is greater than that observed in the local Ordovician source rocks. The Beekmantown hydrocarbons probably migrated from deeper in the Appalachian basin along the Knox unconformity.

Lower Silurian Medina Group gases in northwestern Pennsylvania are late mature and probably originated in Ordovician source rocks. Medina Group gases might be mixtures of thermogenic hydrocarbons, or their geochemistry may indicate reservoir leakage due to gas diffusion through cap rock. Gases produced from structural traps in the Devonian Ridgeley Sandstone and Huntersville Chert of western Pennsylvania are isotopically diverse and reflect both the entrapment of mature associated gases and probable second-order fractionation effects.

Autogenic gases produced from Devonian black shales are postmature along the Allegheny Front and early mature along the northwest basin flank. The early-mature gas is autochthonous and thermogenic.

Most Upper Devonian gases produced across the Plateau are oil-associated gases that were emplaced in reservoirs prior to maximum burial of the Paleozoic section during the Alleghanian orogeny. Some Upper Devonian gases, however, could be residues of diffusive gas leakage or possible mixtures of thermogenic gases that migrated into or from reservoirs located along regional fractures.

Lower Silurian Tuscarora Formation gases produced from fractured sandstones near the Allegheny structural front in central Pennsylvania are postmature hydrocarbons that correlate with local source rocks. Gases produced from fractured Ordovician Bald Eagle Formation rocks near the Allegheny Front, however, are enigmatic. These gases might be postmature hydrocarbons of possible hydrothermal or geothermal origin, or their chemistry could be the result of postgenetic fractionation due to diffusion or oxidation.

Gases produced from bituminous Pennsylvanian coals of the Appalachian Plateau have varied methane δ¹³C and methane δD contents and may be mixtures of thermogenic gas and microbial gas.

INTRODUCTION

Studies of the stable isotope geochemistry of commercial natural gases have increased markedly in recent years (Schoell, 1983, 1988; Whiticar, 1994; Prinzhofer and Huc, 1995; Martini et al., 1996). The stable isotopic composition of methane and other natural gas components can be used to
determine the type and thermal maturity of the organic matter that is the source of the hydrocarbons (Schoell, 1983; Wiese and Kvenvolden, 1993). Stable isotope geochemistry also can help to differentiate original unaltered gases from a single active source rock from gases that are mixtures of different hydrocarbons of varying origins or from gases that were altered through processes such as migration, oxidation, or overprinting with biogenic gas (Schoell, 1983; Whiticar, 1994; Prinzhofer and Huc, 1995).

In this paper, we describe the stable carbon and hydrogen isotope geochemistry of some commercial natural gases from various Paleozoic reservoirs of the Appalachian Plateau in western Pennsylvania and eastern Ohio. The purpose of our reconnaissance investigation was to evaluate the potential use of stable isotope geochemistry for interpreting the origin of these gases and for correlating them with their probable sources. We were particularly interested in comparing our data on gases from deeper portions of the central Appalachian basin with the data on gases from the basin flanks published by Jenden et al. (1993a). We also wished to compare our data with the small quantity of isotopic data from selected Paleozoic gases in Pennsylvania published by Zartman et al. (1961), Wasserburg et al. (1963), Claypool et al. (1978), and Barker and Pollock (1984).

We obtained stable isotope analyses from 27 gas samples (Figure 1; Table 1). Twenty-two samples are from producing gas wells in western Pennsylvania and eastern Ohio. Five samples are from sealed core containers stored at the U.S. Bureau of Mines in Pittsburgh, Pennsylvania, for use in studies of coalbed desorption gases. All samples were analyzed for methane $\delta^{13}C$ and $\delta D$. Ethane $\delta^{13}C$ was determined for ten samples and propane $\delta^{13}C$ was measured in eight samples (Table 2). The isotopic analyses were performed under contract with one of two commercial laboratories, Isotech Laboratories or Krueger Enterprises Geochem Laboratories Division. We also compiled isotopic analyses of Pennsylvania and Ohio natural gases from the literature (Table 3).

**GEOLOGIC SETTING AND HYDROCARBON OCCURRENCES**

The central and southern portions of the Appalachian basin in the eastern United States contain important natural gas resources. Cumulative gas production from the Appalachian basin is estimated as 35 tcf (de Witt and Milici, 1991). Approximately one-third of the gas production, a little more than 11 tcf, is from Paleozoic reservoirs in north-central and western Pennsylvania (Cozart and Harper, 1993). Most of the gas production in Pennsylvania is on the Appalachian Plateau, a gently folded upland that occupies a foreland position northwest of the intensely deformed central Appalachian Ridge and Valley (Gwinn, 1964). Gas fields in eastern Ohio also produce from Paleozoic rocks of the Appalachian Plateau. The Plateau region of southwestern Pennsylvania, eastern Ohio, and northern West Virginia also contains the nation’s third largest in-place coalbed-gas resource (Rice et al., 1993).

Rocks of Cambrian–latest Pennsylvanian and, to a lesser extent, earliest Permian age make up the sedimentary succession of the Appalachian Plateau (Figure 2). In western Pennsylvania, natural gas is produced from about 12 stratigraphic units of Cambrian–Middle Devonian age and from various reservoirs of Upper Devonian age. Some minor production comes from Mississippian and Pennsylvanian age reservoirs, including coalbed accumulations. Most of the gas production in Pennsylvania is from stratigraphic traps in Upper Devonian clastic reservoirs. Only 15% of the state’s cumulative gas production is from deeper reservoirs of Middle Devonian age or older. Most of this deeper production is from Devonian Ridgeley Sandstone and Huntersville Chert reservoirs and from tight gas sand accumulations in the Lower Silurian Medina Group.

The Lower Silurian Medina Group accounts for most of the well completions in Ohio (Cole et al., 1987). Reservoirs in Upper Cambrian and Lower Ordovician rocks, however, are now the principal target of exploratory drilling in that state and are the object of the most active current exploration play in the Appalachian basin.

Potential source rocks in western Pennsylvania include Devonian black shales and the Upper Ordovician Utica Shale and equivalent Antes Shale (Laughrey, 1997). In addition, there are gas-generating coal beds in the Pennsylvanian rocks of the region (Oldham et al., 1993).

The Devonian Ohio and Olentangy shales and the Ordovician Utica and Antes shales are the only widespread rock units in Ohio with adequate organic material to be potential source rocks. TOC (total organic carbon) in the Ohio and Olentangy shales ranges from 0.04 to 10.88 wt. % and averages 1.5 wt. %; TOC in the Utica and Antes shales ranges from 0.00 to 4.23 wt. % and averages 1.3 wt. % (Cole et al., 1987; Wallace and Roen, 1989; Drozd and Cole, 1994). These intervals correlate with the recognized source rocks in western Pennsylvania (Figure 2).

Source rocks in Pennsylvania and eastern Ohio are oil-and-gas prone to gas prone. Devonian source rocks contain type I and type II kerogens that are early mature in northwestern Pennsylvania and east-central Ohio to postmature in west-central and northeastern Pennsylvania along the Allegheny Front (Figure 3A). The Ordovician source rocks are immature along the eastern flanks of the Cincinnati–Findlay arch, but they rapidly increase in maturity as the rocks dip east into the Appalachian basin.
Figure 1—Map of the study area and sample locations in Pennsylvania and Ohio showing the positions of the Allegheny Front and the Cincinnati–Findlay arches. Locations of principal fold axes on the Appalachian Plateau are from Gwinn (1964). Numbers identify the samples in Tables 1 and 2. Samples BP62, BP65, CM, and CL20 are from the literature and are identified in Table 3. OH-9 and OH-33 are geochemical samples from Wallace and Roen (1989).
(Figure 3B). A pod of mature Utica and Antes shale source rocks extends through the subsurface of eastern Ohio and into northwestern Pennsylvania (Cole et al., 1987; Wallace and Roen, 1989; Ryder et al., 1991; Drozd and Cole, 1994). The Antes and Utica shales are postmature, however, across most of the Appalachian Plateau in Pennsylvania. These rocks contain kerogen with no significant hydrocarbon-generating capability.

RESULTS

Methane is the principal component of the gases collected in this study, ranging from 87.2 to 99.4% in our samples (Table 2). Wetness ranges from trace values to 13.2%. The very low wetness values in samples 22–27 in Table 2 are from coalbed gases. A plot of the ratios C2/C3 vs. C1/C2 (from Table 2) using logarithmic scales reveals a steep, almost vertical trend with positive slope (Figure 4). Prinzhofer and Huc (1995) suggested that this trend may indicate that most of these gases derived from secondary cracking of oil. Nitrogen in our samples ranges from less than 1 to 22.8%. Other nonhydrocarbon gases occur only in small quantities.

The methane $\delta^{13}C$ of our samples ranges from −55.1 to −27.24‰ (Table 2). Gases produced from Pennsylvanian coals and Upper Devonian clastic reservoirs display the largest variations in the measurements. Methane $\delta^{13}C$ values of gases produced from Lower Devonian–Upper Cambrian reservoirs exhibit considerably less variability than those produced from younger reservoirs, but there is overlap of the measurements, such as that noted by Hunt (1996). Methane $\delta^{13}C$ increases, for the most part, with increasing geologic age of the reservoirs.

The methane $\delta D$ of our samples ranges from −303 to −150‰. The lightest $\delta D$ value is from methane produced from early-mature Upper Devonian Huron Shale along the Lake Erie shore (sample 16). The heaviest methane $\delta D$ value is from Lower Silurian Tuscarora Formation gas produced at Devil’s Elbow field near the Allegheny structural front (sample 4).

The ten samples for which we measured ethane $\delta^{13}C$ have values ranging from −41.79 to −29.61‰ (Table 2). Eight of these samples have propane $\delta^{13}C$ values of −38.21 to −26.71‰. Two samples, both

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*Gathering system for Spring Creek field.
**Coalbed desorption gas samples.
Table 2. Chemical and Isotopic Data

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<td>1.2</td>
<td>6.7</td>
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<td>-216.0</td>
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<td>25</td>
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<td>26</td>
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<td>Coalbed gas**; %R(_o) = 1.5</td>
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*C\(_2+\) = (1 − C1/ÂCn) 100 (%), from Schoell (1983).

**Coalbed desorption gas samples.
from Lower Devonian Ridgeley Sandstone reservoirs (samples 10 and 11), had insufficient propane for isotopic analyses.

Plots of methane $\delta^{13}C$ vs. methane $\delta D$ indicate a thermogenic origin for most of our gas samples (Figures 5, 6). Most samples evidently originated as wet; i.e., associated gases (see Figures 5, 6) generated from types I and II kerogens at source rock maturities ranging from early mature to postmature. Linear regression of methane $\delta^{13}C$ and $\delta D$ for all the gas well samples in Table 2 yields the equation $\delta D = 3.9 \times \delta^{13}C - 22.5 \%$, which resembles that calculated by Schoell (1983) for thermogenic gases generated from types I and II organic matter ($\delta D = 3.2 \times \delta^{13}C - 25 \%$). Correlation of the samples in our data set, however, is not strong ($r^2 = 0.65$). The regression probably does not reflect entirely the maturation trends of the source material and the gas.

**DISCUSSION**

**Upper Cambrian Reservoirs, Eastern Ohio**

The Rose Run Sandstone produces oil and gas from fault-related traps in southwestern Portage County, Ohio (Riley et al., 1993; Moyer, 1995). Geologic and seismic mapping in this area indicates the presence of a major basement fault, called the Akron-Suffield fault system, trending northwest-southeast beneath the oil and gas field (Figure 1). The Rose Run Sandstone traps in southwestern Portage County probably formed through faulting and fracturing during and subsequent to the development of the Knox unconformity (Riley et al., 1993).

We sampled gas from the Belden and Blake 1 Scruggs well in Portage County, Ohio (sample 1). The well penetrates the downthrown side of one of several small faults that offset the top of the Knox unconformity along the Akron-Suffield fault system (Figure 1). Crossplots of gas wetness vs. methane $\delta^{13}C$, and methane $\delta D$ vs. methane $\delta^{13}C$, indicate a thermogenic, condensate-associated gas generated by oil and kerogen cracking during late catagenesis (Figures 5, 6, 7).

The carbon isotope variations among the methane, ethane, and propane are normal in the Scruggs well; i.e., the methane $\delta^{13}C <$ ethane $\delta^{13}C <$ propane $\delta^{13}C$ (Figure 8). Carbon isotope separations among methane, ethane, and propane fit a level of organic maturity (LOM) of about 11 or a thermal alteration index (TAI) of approximately 3 (James, 1983) (Figure 7). These values correspond to a maturation level equivalent to the late oil window.

Wallace and Roen (1989) published source rock geochemical data from a well just south of the southwestern Portage County producing area and the 1 Scruggs well (OH-33 in Figure 1). TOC and $S_1$ and $S_2$ pyrolysis yields indicate good to very good source rock generative potential for the Utica Shale.

Hydrogen indices and the $S_2/S_3$ ratio from pyrolysis indicate that the Utica Shale is gas and oil prone. $T_{\text{max}}$ and production indices are consistent with late oil window maturation. We believe it is reasonable to conclude that Upper Ordovician black shales several
hundred feet above the Knox unconformity in southwestern Portage County may be the likely source of hydrocarbons in the Rose Sun Sandstone there. 

Erosional remnants of the Beekmantown Dolomite are one of the primary drilling objectives in eastern Coshocton County, Ohio. Reservoirs
occur in zones of solution-enlarged vuggy porosity associated with paleotopographic highs (Riley et al., 1993). We sampled gas from the 1 Mizer well in Coshocton County (sample 2). This well produced 2.6 bcf of gas and 9 million bbl of oil through the end of 1991 (Riley et al., 1993). The 1 Mizer well is on a northwest-southeast–trending structural high associated with the Cambridge arch (Figure 1). The well penetrates the northwest side of a thick (~25 m) paleoremnant of Beekmantown Dolomite.

Plots of gas wetness vs. methane δ¹³C, and methane δ¹³C vs. methane δD for the Mizer well hydrocarbons indicate methane generated in the principal zone of gas-condensate formation during late catagenesis (Figures 5, 6). A plot of the carbon isotope separations between methane, ethane, and propane fit an LOM of about 12 and a TAI of approximately 3 (Figure 8). The estimated thermal maturity of the gas produced from the 1 Mizer well is greater than that of the Utica source rocks in the area. Wallace and Roen (1989) and Ryder et al. (1991, 1995), reported that the conodont alteration index (CAI) of Utica samples in Coshocton County ranges from 1 to 1.5, the average T₉₅ is 440°C, and the average production index (from Rock-Eval pyrolysis) is 0.27. Their data place the Utica Shale in the beginning to middle part of the oil window.

Ryder et al. (1991) noted that the Beekmantown and Rose Run hydrocarbons produced in the Coshocton County area are highly mature, very light oils or condensates that likely were not generated in the less mature, local Utica source rocks. The maturity of their samples is compatible, however, with the level of gas maturation indicated by our isotope data. Ryder et al. (1991) suggested that the highly mature oils were generated in easternmost Ohio or adjoining Pennsylvania and West
Virginia and migrated along the Knox unconformity into traps in eastern and central Ohio. Our stable isotope data support that interpretation.

Lower Silurian Medina Group Reservoirs

Gas fields producing from the Lower Silurian Medina Group in northwestern Pennsylvania and eastern Ohio generally are interpreted as stratigraphic accumulations where facies changes and permeability discontinuities furnish the traps (Laughrey and Harper, 1986). Sandstones in the Medina gas fields are under pressured, tight gas reservoirs. Zagorski (1988) and Law and Spencer (1993) suggested that these under pressured gas accumulations might be basin-centered gas accumulations. Dark shales in the Cabot Head formation of the Medina Group were once surmised to be the source rock for the Medina hydrocarbons (Knight, 1969), but these rocks are organically lean (mean TOC = 0.16% in Pennsylvania) and not likely to have generated commercial quantities of oil or gas. Cole et al. (1987) and Drozd and Cole (1994) correlated hydrocarbons produced from the Medina Group in eastern Ohio with source rocks in the Upper Ordovician Utica and Antes shales. Our Medina gas samples from northwestern Pennsylvania are very mature (samples 5–7). The crossplots of Medina gases in Figures 5 and 6 suggest that these gases are associated with condensate. Our isotope data support previous suggestions that the Utica and Antes shales are the source rock for Medina Group gases in northwestern Pennsylvania, northeastern Ohio, and western New York (Martini, 1971; Jenden et al., 1993a).

The Medina gases plot well above the lines describing the relationships of cogenetic methane, ethane, and propane shown in Figure 7, suggesting a possible mixture of thermogenic gases in the reservoirs. Two of the samples in our database (samples 6 and 7, Table 2) and one from Barkeyville field in Venango County reported by Barker and Pollock (1984) (Table 3) exhibit isotopic reversals between the methane and the ethane. In addition to gas mixing, these isotopic reversals might also suggest oxidation of methane or leakage due to diffusion of gases through the reservoir cap rock (Figure 9).

Devonian Shales

Devonian black shales are major petroleum source rocks in the Appalachian basin (Roen, 1984). These rocks also produce commercial amounts of autogenic gas in southwestern Virginia, eastern Kentucky, southwestern West Virginia, and
southern Ohio (Milici, 1993). The shales also produce gas along the southern shore of Lake Erie from Ohio to New York, but the shales are only marginally productive there (Milici, 1993).

Claypool et al. (1978) used chemical and stable isotope data to determine the regional thermal maturity of organic matter in the Devonian shales of the central Appalachian basin. Claypool et al. (1978) showed that methane $\delta^{13}C$ ratios of the gases increased systematically from lighter values of $-54\%_{oo}$ in central Ohio to heavier values of about $-42\%_{oo}$ near the Allegheny Front in Pennsylvania.

We sampled Devonian shale gas from two wells. One of the gas samples (sample 16) is from the Huron Shale in Erie County, Pennsylvania. The rocks generating this gas are early mature. The Huron methane sample is relatively light, with a methane $\delta^{13}C$ of $-53\%_{oo}$, and with light ethane and propane also (see Table 2). The other gas sample (sample 14) is from postmature shales of the Harrell Formation near the Allegheny Front in Centre County, Pennsylvania. The sample from the Harrell Formation is heavy, with a methane $\delta^{13}C$ of $-38.3\%_{oo}$.

Milici (1993) noted that the Devonian black shale gas fields developed along the south shore of Lake Erie produce from rocks reportedly containing immature organic matter, implying that the gas may have migrated from elsewhere in the Appalachian basin or that it is locally generated microbial gas. Martini et al. (1996) suggested that gas in the Devonian Antrim Shale of the Michigan basin (a correlative of the Huron Shale) originated from the mixing of thermogenic and microbial gases having similar methane $\delta^{13}C$ values. Our data from gas produced at Presque Isle in Erie County,
however, suggest a local, thermogenic origin for the hydrocarbons. The crossplot of methane $\delta^{13}C$ vs. methane $\delta^D$ (Figure 5) indicates an oil-associated gas generated within the early oil window. A plot of the observed carbon isotope separations in the gas vs. source rock LOM implies a TAI of approximately 2 to 2+, which also would denote the early oil window (Figure 8).

Data obtained from Rock-Eval pyrolysis and biomarker analyses of Huron Shale samples from the Erie County well (well 16 in Figure 1) support our interpretation of the gas isotope data. Production indices (0.05–0.10), $T_{\text{max}}$ values (440–441°C), and the ratios of bitumen to total organic carbon (0.058–0.072) all indicate an early oil window. Several biomarker maturation parameters, including $C_{31}$ homohopane isomerization (0.59–0.61), $T_s/(T_s + T_m)$ ratios (0.63–0.65), and both $20S/(20S + 20R)$ and $\beta\beta/(\beta\beta + \alpha\alpha)$ $C_{29}$ sterane isomerization ratios (0.471–0.475 and 0.54–0.56, respectively), also indicate early oil generation (Peters and Moldovan, 1993).

The Harrell Formation gas sample (sample 14) is from Black Moshannon field in Centre County, Pennsylvania. This gas is produced from thin, silty and sandy carrier beds in the upper shale member of the Harrell Formation. Measured TOC in the Burket ranges from 1.34 to 2.13%. Pyrolysis $S_2$ yields are too small (<0.10 mg/g) to obtain production indices or meaningful $T_{\text{max}}$ values, but $R_o$ in the Burket averages 2.45% and TAI averages 3.8. The Burket Shale is postmature. The gas chemistry suggests a relatively mature, condensate-associated gas (Figures 5, 6). The gas isotope data provide a reasonable correlation between the hydrocarbons produced from the upper shale member of the Harrell Formation.
Formation and the source rocks in the Burket Member.

**Lower Devonian Ridgeley Sandstone and Middle Devonian Huntersville Chert**

The Ridgeley Sandstone and Huntersville Chert (Figure 2) comprise the most significant deep-gas reservoirs in western Pennsylvania. These intervals account for almost 80% of all the pre-Late Devonian gas produced there (Harper and Cozart, 1992). Most of this gas is produced from fractured Huntersville Chert and Ridgeley Sandstone on faulted anticlines within isolated fault blocks (Flaherty, 1996).

Ridgeley and Huntersville gases produced at Strongstown and Living Waters fields in Indiana County, Pennsylvania (samples 10–13) plot in the fields of gases associated with condensate (Figures 5, 6). Two of these gases for which we were able to obtain ethane $\delta^{13}$C measurements (samples 10 and 11) exhibit methane $\delta^{13}$C > ethane $\delta^{13}$C. These isotope reversals suggest that the hydrocarbons produced at this field are mixed thermogenic gases, or that the gases are a residue of diffusive gas leakage (Figures 7, 9). We prefer the latter interpretation because Strongstown field lies along the trend of the Home-Gallitzen lineament, a known surface expression of a high-angle subsurface fracture zone (Harper, 1989).

Gas produced from the Seven Springs pool in the Spook Hill field (sample 8) is substantially different from these gases despite the fact that reservoir depths, trap configurations, source rocks, and maturations are similar at all three fields (Laughrey, 1997). Although liquid hydrocarbons are not produced at Spook Hill field, the gas is mature and was generated within the oil window (Figure 5). The gas is very dry (wetness = 1.7%), which is surprising given its methane $\delta^{13}$C composition of $-46‰$. Perhaps this dry methane was originally cogenerated with wet gases and C$_{15+}$ hydrocarbons in the principal oil window, and then left in the reservoir as a methane-rich residue due to intense post-expulsion fractionation of C$_1$–C$_4$ hydrocarbon gases (Price, 1995). Basilone (1984) documented the presence of open fractures in these rocks during the Alleghanian orogeny. These fractures were effective conduits for fluid migration. Basilone (1984) showed that methane-saturated brines and immiscible methane gas were the principal fluids that migrated through these fractures and that ethane, and perhaps even higher homologs, migrated.
through the fractures after they had been open for a considerable period of time.

Sample 9 is from the Svonavec 1 well in the Somerset East field. The methane $\delta^{13}C$ of this gas is $-31.5\%o$, one of our heaviest $\delta^{13}C$ measurements. Crossplots of methane $\delta^{13}C$ vs. wetness and $\deltaD$ (Figures 5, 6) indicate a postmature gas. This interpretation of the gas is supported by the geochemistry of source rock samples analyzed from the Amoco Svetz 1 well west of the Somerset East field. In the Svetz well, Devonian source rocks have an average TAI of 4.2, a mean $R_o$ of 3.28%, and production indices, from Rock-Eval pyrolysis, of 0.63–0.73.

### Upper Devonian Sandstone Reservoirs

All but one of the Upper Devonian sandstone gases that we sampled appear to be early-mature oil-associated gases or mixed microbial and thermogenic gases (samples 17–21, Table 2; Figures 5, 6). Most of these gases are isotopically light. The one exception is gas from the Kane sand of the Bradford Group (sample 17), which appears to be late mature (Figures 5, 6). Other investigators have reported methane $\delta^{13}C$ of $-47$ to $-40.12\%o$ in various gases from Upper Devonian sandstones in western Pennsylvania (Table 3).

The most striking fact about the Upper Devonian sandstone gases is that several light, oil-associated isotopic signatures occur all the way across the Appalachian Plateau regardless of source rock maturity. Figure 10 shows the TAI values of organic matter in the Marcellus Shale along with the well locations and methane $\delta^{13}C$ values of the Upper Devonian gas samples from Tables 2 and 3. The TAI values increase systematically from northwest to southeast across the Plateau. The methane $\delta^{13}C$ values from Devonian shale source rocks also become more mature from northwest to southeast, increasing from about $-54\%o$ along the Lake Erie shore to about $-38\%o$ near the Allegheny Front. Although a few of the methane $\delta^{13}C$ values from Upper Devonian gases correlate with the observed source rock maturity, most of the values do not. The gases along the Allegheny Front are particularly surprising. Here, postmature gases in the Upper Devonian Harrell bear no isotopic resemblance to nearby Upper Devonian sandstone gases.

One possible interpretation of these observations is that gases generated along with oil in the Devonian shale source rocks migrated into many of the Upper Devonian sandstone traps relatively early, before maximum burial and subsequent uplift during the Alleghanian orogeny. Although both oil and gas accumulated in the sandstones, oil was progressively destroyed by thermal degradation during deeper burial, whereas some gases moved away from the oils. Other gases, however, remained trapped in some reservoirs, and their isotopic composition is a
vestige of an earlier genesis within the oil window. Several relevant geologic observations support our hypothesis. Bruner and Smosna (1994) documented the presence of "dead oil" or bitumen in the pore spaces of the Upper Devonian reservoirs producing gas along the Allegheny structural front in Pennsylvania, including the sandstone reservoir that produced the gas we sampled at Council Run field (sample 15, Table 2). Bruner and Smosna (1994) showed that solid bitumen comprises an average of 3% of the bulk composition of these sandstones. They noted 5–10% of the available pore volumes in these sandstones were filled with bitumen. Bitumen coatings in these pores are 0.01–0.02 mm thick and act like clay coatings in the rocks, inhibiting cementation and preserving primary porosity (Bruner and Smosna, 1994). Thus, isotopically light thermogenic methane produced near the Allegheny Front might actually reside in pores preserved by its now-degraded cogenetic oils.

One problem with this interpretation is the fact that isotopically heavier gases, cracked from thermally degraded oils in the reservoirs, should have mixed with the lighter gases generated during the early-mature stage to yield a methane with a less negative δ13C value than that observed at Council Run field. Gas isotope data collected from both nature and laboratory experiments by Price (1995) might help to explain this apparent enigma. Price (1995) argued that methanes with δ13C of −44 to −50‰ possibly contain a significant microbial gas component inherited from in-situ mixing of thermogenic and early microbial methane.

The isotopically heavier gas produced from the Kane sand at Cushion field in Indiana County, Pennsylvania (sample 17) requires a different interpretation. This gas plots in the field for relatively mature oil-associated gases (Figures 5, 6). This gas, however, has an ethane δ13C of −40.88‰ and a propane δ13C of −37.53‰. These are low-maturity δ13C values. Furthermore, the methane, ethane, and propane δ13C values do not exhibit the expected separation for cogenetic gases on Figure 7. The Kane hydrocarbons may represent a mixture of thermogenic hydrocarbons, a gas altered by methane oxidation, or the residue of diffusive gas leakage (Figure 9). We favor the possibilities of methane oxidation or diffusive gas leakage. The Kane sand at Cush Cushion field is a prolific fractured reservoir that lies along the trend of a prominent regional cross-structural discontinuity (Laughrey, 1982; Harper, 1989; Hussing, 1994). A number of geologists have suggested that fluid migration patterns along this discontinuity were iterative and complex throughout the geologic history of the central Appalachian basin (Wheeler, 1980; Rodgers and Anderson, 1984; Harper, 1989).

**Ordovician and Silurian Fractured Reservoirs, Allegheny Structural Front**

The Lower Silurian Tuscarora Formation and the Upper Ordovician Bald Eagle Formation are...
important fractured gas reservoirs near the Allegheny Front in central Pennsylvania. We sampled gases from the Tuscarora Formation at Devil's Elbow field in Centre County (sample 4) and from the Bald Eagle Formation at Grugan field in Lycoming and Clinton counties (sample 3). Potential source rocks along the Allegheny Front in Centre, Lycoming, and Clinton counties are postmature (Figure 3).

The Tuscarora Formation has produced almost 3 bcf of gas from a naturally fractured reservoir at Devil's Elbow field (Harper and Cozart, 1992). The gas is produced from open fractures within tight quartzites. The fractures are propped open by large epigenetic quartz crystals (Wescott, 1982). Isotope data indicate that the Tuscarora Formation gas at Devil's Elbow field is postmature and was generated within the principal zone of gas formation (Figures 5, 6). Gases produced from the Tuscarora Formation at Devil's Elbow correlate with the observed maturity of local Antes Shale source rocks.

Fractured sandstones within the Upper Ordovician Bald Eagle Formation produce gas at one location in the central Appalachian basin, the Grugan field in Pennsylvania. This small field consists of a three-well pool that straddles the border of Clinton and Lycoming counties in the north-central part of the state. Grugan field, its small size notwithstanding, has two of the most productive wells in the entire Appalachian basin. The discovery well, the Pennsylvania State Tract 285, produced 3.6 bcf of gas between the end of 1982 and the end of 1992. The Pennsylvania State Tract 289 well, an extension located about 3.6 km northeast of the discovery well, produced 3.95 bcf of gas between 1985 and the end of 1992.

The gas from the Grugan field has a methane δ¹³C of -27.24‰, the heaviest δ¹³C of any methane ever reported in the Appalachian basin. Crossplots of δ¹³C and δD for the Bald Eagle methane plot outside of the field of most thermogenic gases (Figures 5, 6) and resemble some methanes associated with hydrothermal or geothermal gases (Laughrey and Harper, 1996). Similar to thermogenic gases, most hydrothermal and geothermal methanes probably have an organic source. For example, Des Marais et al. (1981) demonstrated that ¹³C enrichment of geothermal methane with increasing temperature at Yellowstone National Park was due to extensive natural pyrolysis of sedimentary organic matter. Lacazette (1991) proposed that the Bald Eagle Formation in central Pennsylvania, including the reservoir at Grugan field, was fractured by hypersaline, methane-saturated brines that attained superlithostatic pressures during the Alleghanian orogeny. On the basis of fluid inclusion studies, he estimated that fracturing occurred at burial temperatures of 200–205°C. Deep faulting recognized at Grugan field (Henderson and Timm 1985) may have provided migration pathways for such hydrothermal fluids moving out of and through deeper layers, including the Antes Shale source rocks.

The ethane and propane in the Grugan field gas are isotopically lighter than the methane (Table 2). The observed distribution of carbon isotopes in the Grugan methane, ethane, and propane is unusual and superficially resembles that observed in some abiogenic gases (Des Marais et al., 1981; Jenden et al., 1993b); however, the isotopic reversals observed in the gas at Grugan field probably are due to heterogeneities in the source rock organic matter, mixing of gases from different sources, oxidation of thermogenic gas, or partial diffusive leakage of the gas reservoir (Jenden et al., 1993b; Prinzhofer and Huc, 1995) (Figure 9).
Coalbed Gases

The northern Appalachian coal-bearing basin contains an estimated 1730 billion m$^3$ of in-place coalbed natural gas (Rice et al., 1993). Approximately four-fifths of this in-place gas occurs within a concentrated area in southwestern Pennsylvania and northern West Virginia (Diamond et al., 1987). Oldham et al. (1993) published a comprehensive geological report on the coalbed gas production in this region.

We collected six samples of coalbed gases for molecular and isotopic analyses (samples 22–27, Table 2). Sample 22 is from a multilevel completion coalbed gas well in Greene County, Pennsylvania. The other five samples are desorption gases collected from sealed cores of specific coals stored at the U.S. Bureau of Mines laboratories near Pittsburgh, Pennsylvania. Figure 1 shows the original locations of these coal cores. The coals are high-volatile bituminous, with $R_o$ values of these coal cores. The coals are high-volatile bituminous, with $R_o$ values of these coal cores. The coals are high-volatile bituminous, with $R_o$ values of these coal cores. The coals are high-volatile bituminous, with $R_o$ values of these coal cores. The coals are high-volatile bituminous, with $R_o$ values of these coal cores. The coals are high-volatile bituminous, with $R_o$ values of these coal cores.

The $\delta^{13}C$ of coalbed methanes we sampled range from relatively light values of −55.1‰ to as heavy as −39.9‰. The methane $\delta D$ of our coalbed gas samples ranges from −219 to −194‰. Schoell's (1983) plot of methane $\delta^{13}C$ vs. methane $\delta D$, four of the samples appear to be mixtures of thermogenic and microbial methanes, one sample appears to be thermogenic oil-associated gas, and one sample appears to be a dry, nonassociated methane (Figure 5).

The methane $\delta^{13}C$ of coalbed gases is typically lighter (to −60‰) at low ranks and heavier (to −40‰ and greater) at high ranks (Rice et al., 1993). Rice et al. (1993) considered coalbed gases to be both microbial and thermogenic in origin. The principal controls on the molecular and isotopic composition of coalbed gases are the composition and rank of the coal and its depth and temperature history. The composition of coalbed gas also is influenced by secondary processes such as mixing of thermogenic methane with late-stage microbial methane that was generated by anaerobic microorganisms introduced into the coal by groundwater (Rice et al., 1993; Scott et al., 1994).

All of the coals from which we collected gas samples are of relatively high rank and should have generated thermogenic gases. Yet, all but one of our samples (sample 25) have methane $\delta^{13}C$ values lighter than anticipated for coals of the observed rank. We suspect that late-stage microbial gases, generated in the coals by anaerobic microorganisms, are mixed with the thermogenic gases that formed earlier in the coals. Rice et al. (1993) stated that groundwater flow creates a favorable environment for microbial activity and the related generation of late-stage gases. Groundwater movement in the deeper (>50 m) regional aquifer of southwestern Pennsylvania is relatively stagnant due to low hydraulic conductivity of the coal-bearing strata, and the lateral groundwater flow rate is very low (Stoner et al., 1987). Reducing conditions prevail at the depths from which the coalbed gases are produced (Stoner et al., 1987).

Comparisons With Previously Published Gas Data

Jenden et al. (1993a) used stable isotope geochemistry to investigate the origin of commercial natural gases in western and central New York state. They recognized two genetic groups of gases in New York (Figures 5, 6) that they interpreted as mixtures of wet thermogenic gases generated locally in Devonian and Ordovician source rocks and dry post-mature gases that migrated up from deeper portions of the Appalachian basin. Jenden et al. (1993a) presented three principal observations in support of their premise. (1) The range of source rock maturities inferred from stable isotopic compositions of the New York gases is greater than that observed in the Paleozoic rocks of that region. (2) Geochemical parameters, such as gas wetness, methane $\delta^{13}C$, and methane $\delta D$, increase with increasing reservoir age, whereas ethane $\delta^{13}C$ does not. (3) Several gases, especially in Silurian and Ordovician reservoirs, exhibit isotopic reversals (methane $\delta^{13}C >$ ethane $\delta^{13}C$). Jenden et al. (1993a) suggested that their mixing model could be applied to gases in surrounding areas, including the St. Lawrence lowlands, southern Ontario, Ohio, Pennsylvania, and West Virginia. Prinzhofer and Huc (1995), however, examined Jenden et al.’s (1993a) data and noted a good positive correlation of $\delta^{13}C_1$–$\delta^{13}C_2$ vs. $C_1/C_2$, which they interpreted as a straightforward thermogenic trend rather than mixing. Prinzhofer and Huc (1995) interpreted the isotopic reversals in the New York gases to be a postgenetic leakage phenomenon due to diffusion of gases through the cap rock in reservoirs (Figure 9).

The plot of methane $\delta^{13}C$ vs. methane $\delta D$ in Figure 5 suggests that there also are two basic groups of gases in western Pennsylvania and eastern Ohio. One group of gases consists of Pennsylvanian coalbed methanes and Devonian methanes with $\delta^{13}C$ values less than −40‰ and methane $\delta D$ values less than −190‰. This group of hydrocarbons appears to be oil-associated gases or a mixture of microbial and thermogenic gases (Figures 5, 6). A second group consists of Cambrian, Ordovician, Silurian, and Devonian gases with methane $\delta^{13}C$ values greater than −40‰ and methane $\delta D$ greater than 180‰. In Figures 5 and 6, this second group of gases appears to consist of gases
associated with condensate. One of the coalbed gases plots within the field for nonassociated thermogenic methane.

When compared to the data published by Jenden et al. (1993a) (Figures 5, 6), our group of condensate-associated gases is similar to their group II gases. Our oil-associated gases, however, differ markedly from their group I gases. The New York group I gases are much wetter and heavier with respect to methane δ¹³C than are our oil-associated gases. The relative shift from the position of the New York group I gases to our group of oil-associated gases in Figure 6 might indicate that the our group of gases have experienced compositional changes due to shallow migration (Schoell, 1983). Alternately, both this plot and the methane δ¹³C vs. methane δD plot in Figure 5 also suggest that our group of oil-associated gases might be mixtures of microbial and thermogenic gases.

CONCLUSIONS

Stable isotope geochemistry provides some insight into the origin of natural gases in western Pennsylvania and eastern Ohio, and provides some information concerning the timing and direction of gas migration into different reservoirs. The data suggest that most of the gases have multiple sources or were altered by geological or biogeochemical processes. Gas mixing, oxidation, and diffusive leakage from reservoirs are processes that may have affected the gases during their geological history.

In eastern Ohio, gases in Rose Run Sandstone reservoirs probably are derived from adjacent Ordovician source rocks, whereas gases in Beekmantown Dolomite reservoirs are probably derived from deeper downdip source rocks. Gases in Ordovician, Silurian, and possibly Lower-Middle Devonian reservoirs appear to have a mixed origin with an overprint of an isotopically heavy, dry gas derived from deeper parts of the Appalachian basin. An alternate interpretation is that these gases bear the isotopic signature of second-order fractionation effects and are residues of diffusive leakage of gases through cap rocks. We favor the latter interpretation for gas accumulations in reservoirs located along regional subsurface fracture zones. Several Upper Devonian reservoir gases in western Pennsylvania most likely migrated into reservoirs relatively early in their burial history. Coalbed gases in Pennsylvania are dry gases with a probable overprint of secondary microbial methane.

We conclude this paper by reminding readers that this was a reconnaissance investigation designed to evaluate the potential utility of stable isotope geochemistry for interpreting the origin of natural gases in portions of the central Appalachian basin and for correlating the gases with their probable sources. We believe that a much larger database will be needed to support, verify, or refute our observations and interpretations. We are satisfied, however, that the techniques and data presented here do indeed sustain the information and conclusions of several other workers who have studied the origins of gases in the Appalachian basin, and we are convinced that isotope geochemistry could serve as an important tool for discovering new reserves in this mature basin.

REFERENCES CITED


Gas Origins, Appalachian Basin


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