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GEOLOGICAL SURVEY

# OCCURRENCE AND ORIGIN OF NATURAL GAS IN GROUND WATER, SOUTHERN WELD COUNTY, COLORADO

By


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ILLUSTRATIONS

Occurrence and Origin of Natural Gas in Ground Water,
Southern Weld County, Colorado

By
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## INTRODUCTION

This report deals with the occurrence and origin of methane-rich gas in ground water in the southern part of Weld County, north-central Colorado. The gas generally occurs in solution in the ground water of the aquifer. However, exsolution resulting from reduction of hydrostatic pressure during water production may create free gas which can accumulate in wells and buildings and pose an explosion and fire hazard. On the basis of evidence discussed below, we conclude that the gas originates within the aquifer from the microbiological degradation of organic matter.

The ground water is produced from siltstones and sandstones which make up the Upper Cretaceous Laramie-Fox Hills aquifer (Robson and others, 1981). The aquifer is present at depths of about 150 m or less in the study area. The Laramie-Fox Hills aquifer is an important source of water for residents and ranches in the greater Denver area.

The gas-bearing aquifer of the Laramie-Fox Hills is underlain by the Wattenberg field which contains major reserves of natural gas at depths ranging from 2,300 to 2,600 m. Reservoirs are low-permeability sandstones of Early Cretaceous age that require massive hydraulic stimulation to provide economic flow rates. Reserves in the field are estimated to be 1.5 trillion cubic feet (Matuszczak, 1973).

Natural gas is formed by two distinct processes. At shallow depths of burial and low temperatures, methane-rich gas is generated during decomposition of organic matter by microorganisms. This gas is formed in environments free of dissolved oxygen and sulfate and is referred to as biogenic gas.

Natural gas can also be generated by thermal degradation and cracking of kerogen and other nonhydrocarbon precursors with increasing temperature and advancing geologic time. This type of gas is referred to as thermogenic and probably is the origin of most gas produced from commercial oil and gas fields.

Natural gases can generally be distinguished by their chemical compositions and carbon isotope ratios. Biogenic gas is predominantly methane that is isotopically light ($\delta^{13}C$ values lighter than -55 ppt) because of biological $^{12}C$-enrichment (Rice and Claypool, 1981). During early and intermediate stages of thermal history, methane generation is accompanied by heavier hydrocarbons including oil and is isotopically heavier than biogenic gas ($\delta^{13}C_1$ values are generally heavier than -50 ppt) because of smaller kinetic isotope effects associated with thermal cracking. During late stages of burial history at very high temperatures, natural gas becomes devoid of all heavier hydrocarbons and the isotopic composition of methane approaches that of the original organic matter ($\delta^{13}C$ values are generally heavier than -35 ppt).

In order to determine the source of the gas in the ground water in southern Weld County, natural gas was sampled and analyzed from three private water wells and three gas wells from the Wattenberg gas field. All of the wells are located within a small area (secs. 12, 13, and 24, T. 3 N., R. 65 W.). Samples were analyzed by the methods described by Claypool and others (1980).

## RESULTS AND DISCUSSION

The analyses for the water and gas wells are summarized in Tables 1 and 2, respectively. The volume percentage of selected components is reported together with the proportion of methane in the hydrocarbon fraction and the carbon isotope ratio of the methane.

The gases from the water wells occur at depths of less than 125 m, and are uniformly dry ($C_1/C_{1-5} > 0.99$) and enriched in the light isotope $^{12}C$ ($\delta^{13}C_1$ values are about -73 ppt) (Table 1). The relatively high percentage of $N_2$ (nitrogen) and (or) air probably represents air contamination resulting from sampling procedures. These gases are interpreted to be of biogenic origin and are being (were) generated in an anoxic, sulfate-free environment within the aquifer system. The probable source of carbon is the organic matter originally deposited with the Upper Cretaceous sediments. These biogenic gases are similar in composition to those from ground water reported by Coleman and others (1977) and Barker and Fritz (1981).

In an area immediately north of the study area, methane generally is not detected or reported from ground water (J. C. Romero, oral commun., 1982). This area coincides with a region of higher amounts of dissolved sulfate (greater than 250 milligrams per liter) in the ground water (Robson and others, 1981). The water from the wells in this region has a putrid odor and probably contains hydrogen sulfide ($H_2S$) resulting from microbial sulfate reduction. Methanogenesis generally is not concurrent with the process of sulfate reduction and usually begins after dissolved sulfate is removed from ground water (Claypool and Kaplan, 1974). Therefore, the absence of methane and the apparent presence of $H_2S$ in the area to the north of the study area is probably explained by the occurrence of sulfate.

Gases sampled from the Wattenberg field occur at considerably greater depths (about 2,300 m) and are distinctly different from gas from water wells in both chemical and isotopic composition (Table 2). They contain significant amounts of heavier hydrocarbons ($C_1/C_{1-5}$ values are about 0.87) and are isotopically heavier ($\delta^{13}C_1$ values are about -43 ppt). The chemical and isotopic composition of the gases indicate that they are thermogenic in origin and were generated by thermal cracking processes during intermediate stages of thermal maturity in the deeper part of the Denver Basin. This interpretation is consistent with the level of maturation determined by Clayton and Swetland (1980) in their study of petroleum generation in the Denver Basin.

The possibility that thermogenic gas from deeper reservoirs in the Wattenberg field may have leaked into shallow ground water of Laramie-Fox Hills aquifer has been discounted. Several field studies have shown that although chemical fractionation of gas by migration is possible, with nearly complete removal of heavier hydrocarbons, there is no significant effect on the isotopic composition of the methane (Bernard and others, 1977; Coleman and others, 1977; Rice, 1980). Therefore, we conclude that in this case the isotopic analysis is the most reliable evidence to establish the source of the natural gas.

In conclusion, selected gases from ground water and from deeper gas reservoirs in southern Weld County, Colorado are: (1) separated vertically by 2,000 m of rock, (2) have distinct chemical and isotopic compositions, and (3) were formed by two separate processes. The isotopically light, methane-rich gas in the ground water is of biogenic origin and was or is being generated in the anoxic, sulfate-free aquifer by decomposition of organic matter deposited with the sedimentary rocks that constitute the aquifer. In contrast, isotopically heavy, chemically wet gas of the Wattenberg field is clearly of thermogenic origin resulting from sedimentary organic matter that was subjected to increased temperatures and depths of burial. The possibility of leakage of thermogenic gas into the shallow ground water system is discounted because of the distinct and characteristic isotopic compositions of the two types of gases and because subsurface migration is incapable of producing the required change in isotopic composition.

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Table 1.--Chemical and isotopic composition of gas from private water wells.

| Location | Total depth (m) | $C_1$ | $C_2$ | $CO_2$ | $N_2$-air | $C_1/C_{1-5}$ | $\delta^{13}C_1$ (ppt) |
|---|---|---|---|---|---|---|---|
| 1. SW 1/4 SW 1/4 sec. 12, T. 3 N., R. 65 W. | 122 | 28.18 | .04 | .03 | 71.75 | .9989 | -73.5 |
| 2. SE 1/4 NE 1/4 sec. 13, T. 3 N., R. 65 W. | 95 | 51.19 | .06 | .33 | 48.42 | .9988 | -73.3 |
| 3. SE 1/4 SE 1/4 sec. 13, T. 3 N., R. 65 W. | 94 | 56.00 | .07 | .18 | 43.75 | .9988 | -72.8 |

Table 2.--Chemical and isotopic composition of gas from wells in Wattenberg gas field.

| | Well Name | Location | Pay zone (m) | $C_1$ | $C_2$ | $C_3$ | $_iC_4$ | $_nC_4$ | $_iC_5$ | $_nC_5$ | $CO_2$ | $N_2$-air | $C_1/C_{1-5}$ | $\delta^{13}C_1$ (ppt) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | Amoco UPRR 39 B No. 1 | SW 1/4 sec. 13, T. 3 N., R. 65 W. | 2314-2322 | 82.66 | 7.81 | 2.39 | .73 | .73 | .33 | .25 | 4.72 | .38 | .8711 | -43.1 |
| 2. | Amoco Weld Co. Lumber No. 1 | SW 1/4 NE 1/4 sec. 24, T. 3 N., R. 65 W. | 2305-2318 | 82.75 | 7.94 | 2.6 | .5 | .57 | .37 | .24 | 4.63 | .4 | .8714 | -43.4 |
| 3. | Amoco Gurtler No. 1 | SW 1/4 SW 1/4 sec. 24, T. 3 N., R. 65 W. | 2310-2331 | 82.72 | 8.19 | 2.18 | .53 | .53 | .55 | .33 | 4.54 | .43 | .8704 | -43.5 |

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

# NATURE AND ORIGIN OF "VENT GASES" IN THE LASALLE AREA, NORTHEASTERN COLORADO



By

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April Vuletich

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ILLUSTRATIONS

# Nature and Origin of "Vent Gases" in the LaSalle Area, Northeastern Colorado

by

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Charles N. Threlkeld
April Vuletich

## INTRODUCTION

Recently, natural gas has been venting to the surface in the town of LaSalle, southern Weld County, Colorado. The gas is believed to be coming up abandoned water wells that may be as much as 335 m (1100 ft) deep. The gas has reportedly caused explosions in the yard of Wickes Lumber Company and may result in more explosions in the future if the flow of gas from the subsurface continues. Our investigations are aimed at determining the source of the gas. Based on evidence presented below, the gas is interpreted to be of thermogenic origin and to have migrated from deeper, thermally mature rocks.

LaSalle is in the Wattenberg area, which lies along the axis of the Denver Basin. Hydrocarbons are produced in the area from three main reservoirs of Cretaceous age that range in depth from 1220 m (4000 ft) to 2590 m (8500 ft).

Natural gas also occurs in ground water of the Upper Cretaceous Laramie-Fox Hills aquifer in the region at depths less than 150 m (500 ft). Pumping the water to the surface lowers the pressure and causes dissolved gas to come out of solution. If the free gas accumulates in an enclosed area, it can cause an explosion and fire hazard.

Natural gas is formed by two distinct processes. At shallow depths of burial and low temperatures, methane-rich gas is generated during decomposition of organic matter by microorganisms. This gas is formed in environments free of dissolved oxygen and sulfate and is referred to as biogenic gas.

Natural gas can also be generated by thermal degradation and cracking of kerogen, oil, and other nonhydrocarbon precursors with increasing temperature and advancing geologic time. This type of gas is referred to as thermogenic and probably is the origin of most gas produced from commercial oil and gas fields.

Natural gases can generally be distinguished by their chemical compositions and carbon isotope ratios (Fuex, 1977). Biogenic gas is predominantly methane that is isotopically light ($\delta^{13}C_1$ values lighter than -55 ppt) because of biological $^{12}C$-enrichment (Rice and Claypool, 1981). During early and intermediate stages of thermal history, methane generation is accompanied by heavier hydrocarbons, including oil, and is isotopically heavier than biogenic gas ($\delta^{13}C_1$ values are generally heavier than -50 ppt) because of smaller kinetic isotope effects associated with thermal cracking. During late stages of burial history at very high temperatures, natural gas becomes devoid of all heavier hydrocarbons and the isotopic composition of methane approaches that of the original organic matter ($\delta^{13}C_1$ values are generally heavier than -35 ppt).

In order to determine the origin of "vent" gas at LaSalle, natural gas was sampled and analyzed from six sites in the area of Wickes Lumber Company (sec. 31, T. 5 N., R. 65 W.) and from nearby oil and gas wells. Samples were analyzed by the methods described by Claypool and others (1980).

## RESULTS AND DISCUSSION

The analyses are summarized in Tables 1 and 2. The volume percentage of selected components is reported, together with the proportion of methane in the hydrocarbon fraction and the carbon isotope ratio of the methane.

The results of other gas studies in the general area by Rice and Threlkeld (1982) and Rice (1983a) are important in determining the origin of the "vent" gases at LaSalle. Natural gases from water wells near Hudson (secs. 12 and 13, T. 3 N., R. 65 W.) are generally dry ($C_1/C_{1-5}$>0.99) and enriched in the light isotope $^{12}C$ ($\delta^{13}C_1$ values are about -73 ppt) (Rice and Threlkeld, 1982). These gases were interpreted to be of biogenic origin and are being or were generated in an anoxic, sulfate-free environment within the aquifer system.

Natural gases from the Terry and Hygiene Sandstone Members of Pierre Shale, Codell Sandstone Member of Carlile Shale, and "J" sandstone have been sampled and analyzed in the Wattenberg area, which includes LaSalle (Rice, 1983a). These gases, on the basis of chemical and isotopic composition, are interpreted to be of thermogenic origin; that is, the gas was generated during the mature stage of hydrocarbon generation (Fig. 1).

Gases from the Terry and Hygiene Sandstone Members of the Pierre Shale, the youngest reservoirs, are the isotopically lightest ($\delta^{13}C_1$ values range from -55.7 to -47.7 ppt) and chemically wettest ($C_1/C_{1-5}$ values range from 0.67 to 0.83) (Fig. 2) and are associated with oil. Because the Pierre Shale is not exceptionally organic-rich and is marginally mature in the area, the oil and gas in the Terry and Hygiene have probably migrated vertically as much as 610 m (2000 ft) from the thermally mature Greenhorn-Niobrara interval.

Gases from the Codell generally become isotopically heavier ($\delta^{13}C_1$ values range from -47.8 to -43.5 ppt) as they become chemically drier ($C_1/C_{1-5}$ values range from 0.76 to 0.8) (Fig. 2). During the main part of mature stage, oil and associated gas (isotopically lightest and chemically wettest) were generated from Type II kerogen associated with thermally mature marine source rocks, such as those in Greenhorn-Niobrara interval. During the hotter, later part of the stage, wet gas (isotopically heaviest and chemically driest) and condensate were generated from residual kerogen and from heavier hydrocarbons previously generated.

Variations in the character of the gases from the "J" sandstone, the oldest reservoir, are similar to those of the Codell; they become isotopically heavier ($\delta^{13}C_1$ values range from -47.9 to -43.1 ppt) as they become chemically drier ($C_1/C_{1-5}$ values range from 0.84 to 0.87) (Fig. 2). Gases from "J" are interpreted to have been generated at similar levels of maturity as those of the Codell, but from nonmarine (Type III) kerogen closely associated with the reservoirs. These gases are nonassociated and are isotopically heavier and chemically drier at similar levels of maturity than those generated from marine source rocks (Rice, 1983b).

The "vent" gases at LaSalle are chemically wet ($C_1/C_{1-5}$ values of about 0.8) and isotopically heavy ($\delta^{13}C_1$ values of about -44 ppt) (Table 1), and are interpreted to be of thermogenic origin. The gases are almost identical in compositon to those produced from the underlying Codell Sandstone Member in the immediate area and in the Wattenberg area (Tables 1 and 2; Fig. 2). The only exception is that the gas from the Dabco No. 2 well has as much as 20% $CO_2$ (Fig. 2). The $CO_2$ was probably added to the well during its recent hydraulic stimulation required to provide economic flow rates.

In conclusion, the "vent" gases at LaSalle are almost identical in both chemical and isotopic compostion to those produced from the Codell Sandstone Member of Carlile Shale at depths of about 2130 m (7000 ft). The gas was probably generated from thermally mature marine source rocks (Type II kerogen) in the Greenhorn-Niobrara interval and has subsequently migrated to the surface. At this time, we do not have data to determine if this gas migration is a natural phenomenon or is related to drilling activity in the area.

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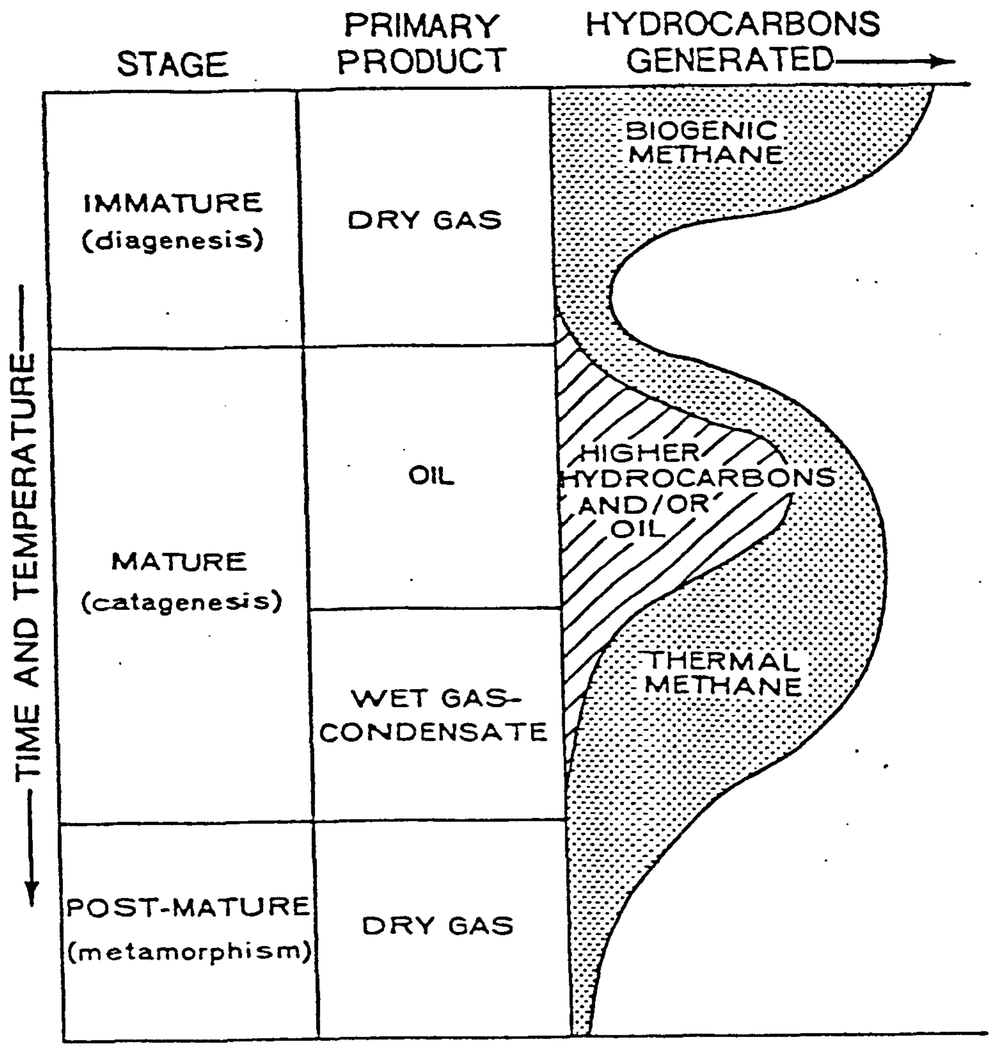


Figure 1. Diagram showing postulated generation of hydrocarbons with increasing temperature and time.

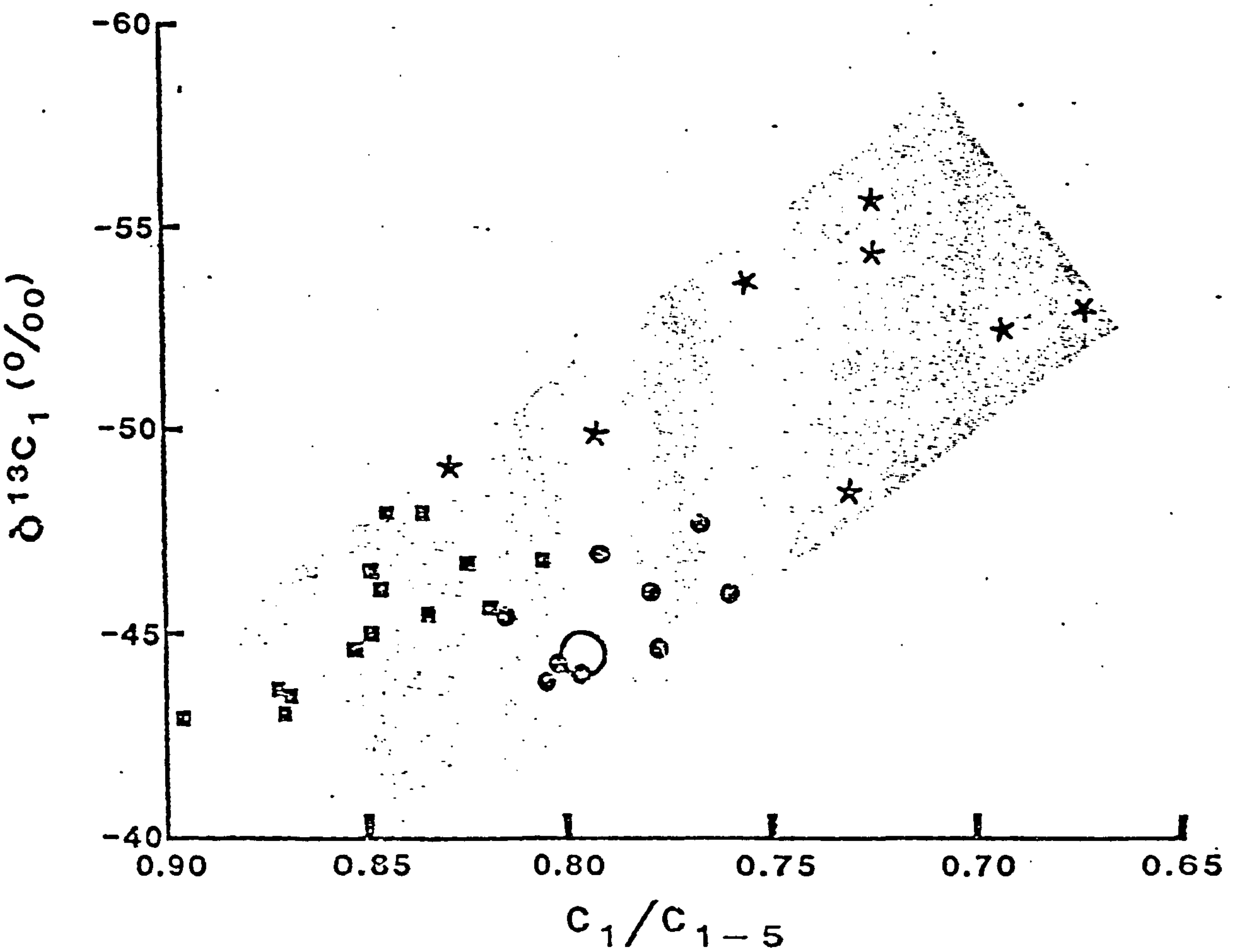


Figure 2. Hydrocarbon composition versus methane carbon isotope ratio of natural gas from Wattenberg area, Denver Basin. Stars indicate gas samples from Terry and Hygiene Sandstone Members, Pierre Shale; dots from Codell Sandstone Member, Carlile Shale; squares from "J" sandstone. Circle indicates "vent" gases from LaSalle.

Table 1.--Chemical and isotopic composition of "vent" gas from LaSalle.

| | | $C_1$ | $C_2$ | $C_3$ | $_iC_4$ | $_nC_4$ | $_iC_5$ | $_nC_5$ | $CO_2$ | $N_2$-air | $C_1/C_{1-5}$ | $\delta^{13}C$ (ppt) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | Abandoned Well | 73.56 | 11.97 | 4.77 | 0.92 | 1.5 | 0.6 | 0.61 | 1.07 | 5.01 | .7932 | -44.42 |
| 2. | Sewer Line Exit | 75.65 | 11.98 | 4.36 | 0.76 | 1.66 | 0.48 | 0.51 | 1.55 | 3.06 | .7931 | -44.[illegible]5 |
| 3. | "Vent" Hole No. 3 | 75.65 | 12.29 | 4.47 | 0.7 | 1.3 | 0.32 | 0.32 | 1.54 | 3.42 | .796 | -44.38 |
| 4. | "Vent" Hole | 76.00 | 12.44 | 4.48 | 0.72 | 1.32 | 0.34 | 0.35 | 1.71 | 2.62 | .7944 | -44.44 |
| 5. | "Vent" Hole | 66.87 | 10.62 | 3.73 | 0.59 | 1.04 | 0.28 | 0.28 | 2.34 | 14.25 | .8017 | -44.96 |
| 6. | "Vent" Hole | 73.75 | 12.37 | 4.54 | 0.69 | 1.19 | 0.32 | 0.32 | 1.71 | 5.1 | .7914 | -44.42 |

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Table 2.--Chemical and isotopic composition of gas from nearby oil and gas wells.

| | $C_1$ | $C_2$ | $C_3$ | $_iC_4$ | $_nC_4$ | $_iC_5$ | $_nC_5$ | $CO_2$ | $N_2$-air | $C_1/C_{1-5}$ | $\delta^{13}C_1$ (ppt) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Lehan No. 1<br>Sec. 8, T. 4 N., R. 65 W.<br>Codell Ss. Mbr.<br>2167-2171 m<br>(7111-7123 ft) | 32.03 | 4.97 | 1.92 | 0.29 | 0.42 | 0.15 | 0.12 | 0.96 | 59.15 | .8030 | -44.38 |
| 2. Dabco No. 2<br>Sec. 6, T. 4 N., R. 65 W.<br>Codell Ss. Mbr.<br>2176-2182 m<br>(7140-7160 ft) | 66.12 | 11.61 | 3.6 | 0.76 | 1.08 | 0.37 | 0.29 | 16.03 | 0.16 | .7889 | -43.47 |
| 3. Dabco No. 2<br>Sec. 6, T. 4 N., R. 65 W.<br>Annular gas | 66.46 | 9.94 | 3.15 | 0.59 | 1.0 | 0.28 | 0.26 | 20.98 | 0.34 | .8066 | -43.90 |
| 4. McClintock No. 6<br>Sec. 32, T. 4 N., R. 65 W.<br>Terry Ss. Mbr.<br>1405-1410 m<br>(4611-4627 ft) | 70.50 | 10.86 | 7.42 | 1.79 | 3.13 | 1.2 | 1.21 | 0.61 | 3.29 | .7336 | -47.73 |
| 5. Aristocrat No. 1<br>Sec. 5, T. 3 N., R. 65 W.<br>Terry Ss. Mbr.<br>1378-1385 m<br>(4522-4545 ft) | 74.56 | 8.04 | 6.82 | 1.5 | 2.13 | 0.61 | 0.72 | 0.77 | 4.84 | .7899 | -50.29 |