# Sources and Migration Pathways of Natural Gas in Near-Surface Ground Water Beneath the Animas River Valley, Colorado and New Mexico

by Daniel T. Chafin

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**[Plates are in pocket]**



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## CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

| Multiply | By | To obtain |
|---|---|---|
| acre | 0.4047 | hectare |
| cubic foot ($ft^3$) | 0.028317 | cubic meter |
| foot (ft) | 0.3048 | meter (m) |
| gallon per minute (gal/min) | 3.785 | liter per minute |
| inch (in) | 2.54 | centimeter |
| mile (mi) | 1.609 | kilometer |
| pound per square inch ($lb/in^2$) | 6.895 | kilopascal |
| pound per square inch per foot [($lb/in^2$)/ft] | 22.62 | kilopascal per meter |
| square mile ($mi^2$) | 2.589 | square kilometer |

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

°F = 9/5(°C)+32.

Degree Fahrenheit (°F) may be converted to degree Celsius (°C) by using the following equation:

°C = 5/9(°F-32).

**Sea level:** In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Other abbreviations, terms, and symbols used in this report:

centipoise (cP)

degrees Fahrenheit per 100 feet (°F/100 ft)

grams per cubic centimeter ($g/cm^3$)

microsiemens per centimeter at 25 degrees Celsius (µS/cm)

milligrams per liter of gas ($mg/L_g$)

milligrams per liter of water (mg/L)

permil (‰)

## GLOSSARY

Natural-gas and gas-well terms are defined in the GLOSSARY and are italicized when first used in this report.

*annulus*.--Open volume between wall(s) of drill hole(s) and a gas-well casing (or gas-well-casings) (plural is *annuli).*

*biogenic gas*.--Gas (mostly methane) that is generated by bacterial processes at relatively small temperatures and pressures.

*bradenhead*.--An impermeable steel housing that caps the open space between the surface casing and the intermediate or production casing of a gas well and that is used to monitor the presence of gas in the surface casing.

*cathodic-protection well*.--A coke-filled drill hole that protects a gas-well casing from corrosion; typically drilled several hundred feet deep and within several hundred feet of a gas well.

*coal-bed gas well*.--A gas well that produces gas by dewatering of coal beds (in this report, those of the Fruitland Formation).

*conventional gas well*.--A gas well that produces separate-phase gas that is trapped in geologic strata by buoyant forces.

*intermediate casing*.--A gas well casing that is installed to intermediate depth and contains the production casing.

*production casing*.--A gas-well casing that transports gas from the producing formation to the land surface.

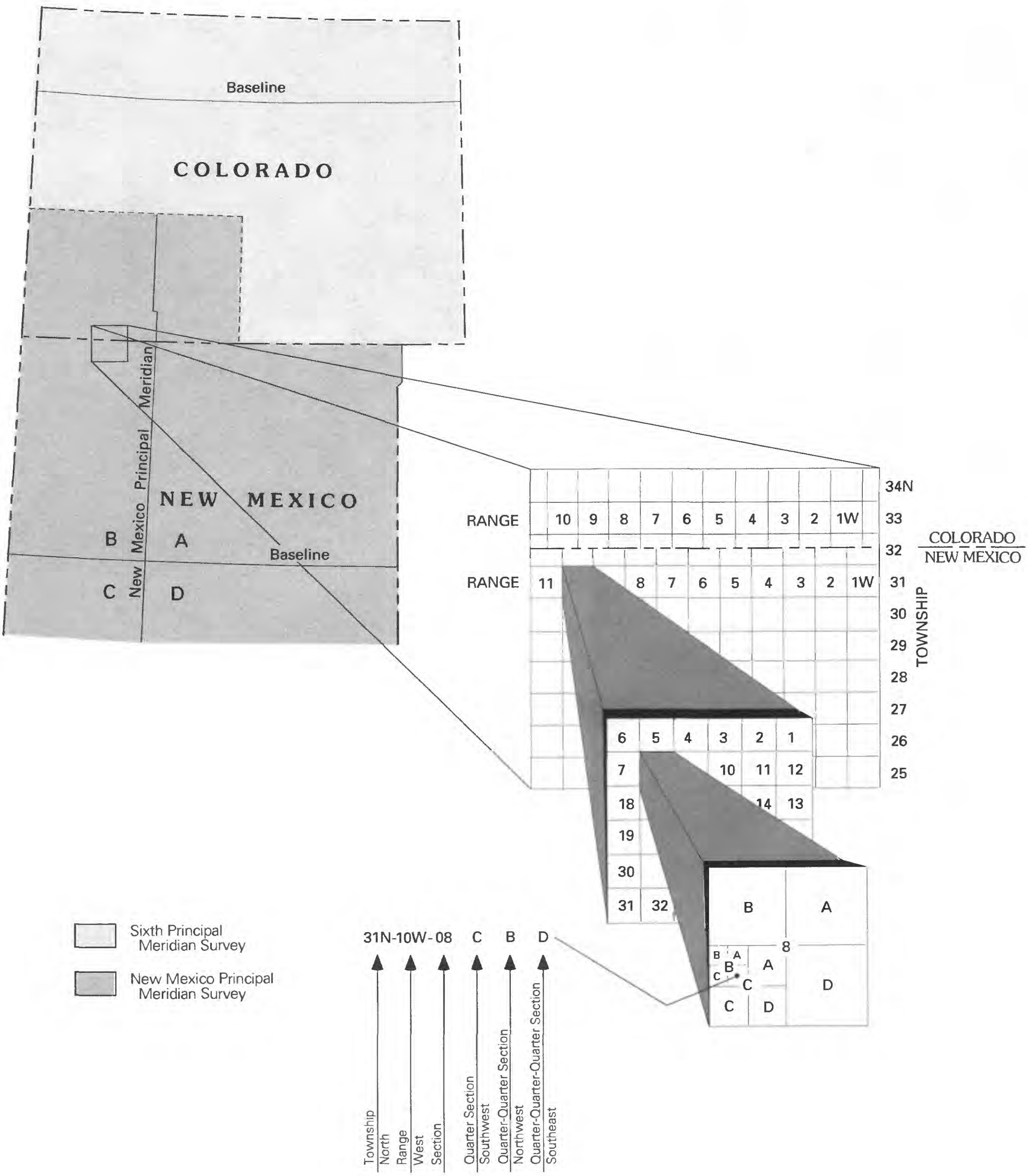
*surface casing*.--A gas-well casing that is cemented against the earth and protects near-surface aquifers from gas and water that might invade the annulus.

*thermogenic gas*.--Gas that is generated by elevated temperatures and pressures generally associated with deep burial of sediments over substantial periods of time.

## SYSTEM OF NUMBERING WELLS

Well locations (land-net locations) listed in this report are based on the U.S. Bureau of Land Management system of land subdivision and indicate the position of the wells by township, range, section, and position within the section. This method of well location is shown in the figure on the following page. All of the locations in this report are north of the New Mexico baseline and west of the New Mexico principal meridian.

The land-net system indicates location by using three numbers followed by two to four letters. The first number indicates the township; the second number, the range; and the third number, the section in which the well is located. The letters following the section number indicate the location of the well within the section. The first letter usually denotes the quarter section; the second, the quarter-quarter section; and the third, the quarter-quarter-quarter section. The letters are assigned within the section in a counterclockwise direction, beginning with A in the northeastern quarter (NE 1/4) and followed by B in the northwestern quarter (NW 1/4), C in the southwestern quarter (SW 1/4), and D in the southeastern quarter (SE 1/4). Letters are assigned within each quarter section and within each quarter-quarter section in the same manner. The final letter "X" indicates that the well is centered in the smallest section subdivision listed. Map locations in irregular sections were derived by alignment of the section template at the southeastern corner and along the southern boundary of the section and extending template subdivisions into uncovered section areas where necessary. For example, 31N-10W-08CBD indicates a well inventoried in the SE 1/4 of the NW 1/4 of the SW 1/4 of section 8, Township 31 North, Range 10 West.



Baseline
COLORADO
NEW MEXICO
New Mexico Principal Meridian
B
A
C
D
Baseline
RANGE
10 9 8 7 6 5 4 3 2 1W
RANGE
11 8 7 6 5 4 3 2 1W
34N
33
32
31
30
29
28
27
26
25
TOWNSHIP
COLORADO
NEW MEXICO
6 5 4 3 2 1
7 10 11 12
18 14 13
19
30
31 32
B A
8
D
C D
Sixth Principal Meridian Survey
New Mexico Principal Meridian Survey
31N-10W-08 C B D
Township North
Range West
Section
Quarter Section Southwest
Quarter-Quarter Section Northwest
Quarter-Quarter-Quarter Section Southeast

# Sources and Migration Pathways of Natural Gas in Near-Surface Ground Water Beneath the Animas River Valley, Colorado and New Mexico

*By* Daniel T. Chafin

## Abstract

In July 1990, the U.S. Geological Survey began a study of the occurrence of natural gas in near-surface ground water in the Animas River valley in the San Juan Basin between Durango, Colorado, and Aztec, New Mexico. The general purpose of the study was to identify the sources and migration pathways of natural gas in near-surface ground water in the study area. The purpose of this report is to present interpretive conclusions for the study, primarily based on data collected by the U.S. Geological Survey from August 1990 to May 1991.

Seventy of the 205 (34 percent) ground-water samples collected during August-November 1990 had methane concentrations that exceeded the reporting limit of 0.005 milligram per liter. The maximum concentration was 39 milligrams per liter, and the mean concentration was 1.3 milligrams per liter. Samples from wells completed in bedrock have greater mean concentrations of methane than samples from wells completed in alluvium. Correlations indicate weak or nonexistent associations between dissolved-methane concentrations and concentrations of dissolved solids, major ions, bromide, silica, iron, manganese, and carbon dioxide. Dissolved methane was associated with hydrogen sulfide.

Soil-gas-methane concentrations were measurable at few of 192 ground-water sites, even at sites at which ground water contained large concentrations of dissolved methane, which indicates that soil-gas surveys are not useful to delineate areas of gas-affected ground water. The reporting limit of 0.005 milligram per liter of gas was equaled or exceeded by 40 percent of soil-gas measurements adjacent to 352 gas-well casings. Concentrations of at least 100 milligrams per liter of gas were measured at 25 (7 percent) of the sites.

Potential sources of gases in water, soil, gas-well surface casings, and cathodic-protection wells were determined on the basis of their isotopic and molecular compositions and available information about gas-well construction or leaks. Biogenic and thermogenic sources of gas exist in the near-surface environment of the study area. Biogenic gas is present locally in the near-surface Animas and Nacimiento formations, and biogenic gas has been detected in water wells completed in those rocks. Most gas probably is thermogenic gas from deep reservoirs, including the Dakota Sandstone, Mesaverde Group, Lewis Shale, Pictured Cliffs Sandstone, and coals in the Fruitland Formation. Less important sources include sandstones in the upper Fruitland Formation and the Kirtland Shale.

Although migration of gas by diffusion or through natural fractures is possible, manmade conduits probably account for most of the upward migration of gas to the near-surface environment of the study area. Primary migration pathways largely consist of 1) leaking, conventional gas wells and 2) uncemented annuli of conventional gas wells along coals in the Fruitland Formation. Secondary migration pathways are gas-well annuli, cathodic-protection wells, seismic-test holes, and bedrock water wells.

## INTRODUCTION

Shallow ground water contains natural gas in parts of the San Juan Basin that are underlain by gas-bearing rocks of Cretaceous age. Domestic water supplies are obtained from aquifers in rocks and alluvium of Tertiary age overlying Cretaceous rocks. Recent development of methane from coal beds of the Fruitland Formation in the San Juan Basin has caused public concern about the possibility of increasing concentrations of natural gas in domestic water supplies. The Animas River valley, one of the most populated areas in the San Juan Basin, is underlain by productive gas fields of the Fruitland Formation and other rocks. In July 1990, the U.S. Geological Survey began a study of the occurrence of natural gas in ground water in the Animas River valley between Durango, Colorado, and Aztec, New Mexico (fig. 1). This study was done in cooperation with the Colorado Oil and Gas Conservation Commission (COGCC), La Plata County, Colorado, and the Southern Ute Tribal Council. Existing data were provided by the New Mexico Oil Conservation Division (NMOCD), the Gas Research Institute, and Amoco Production Company.

The purpose of the study was to identify the sources and migration pathways of natural gas in near-surface ground water in the Animas River valley. The specific objectives of the study were to:

(1) Map the occurrence of methane in near-surface ground water;

(2) Assess the current chemical quality of near-surface ground water and evaluate the potential for upward movement of water containing large concentrations of dissolved-solids; and

(3) Determine possible sources and pathways of migration for natural gas in near-surface ground water.

Sources could include bacterial processes at shallow depths, indigenous thermogenic gas in near-surface aquifers, or thermogenic gas from deep gas-yielding reservoirs. Pathways to the near-surface environment could include upward diffusion through rock pore spaces, migration along natural fractures, leaking gas wells, gas-well annuli, and other manmade conduits.

## Purpose and Scope

This report presents an assessment of the sources and migration pathways of near-surface natural gas. This assessment is based on:

(1) Relations of dissolved-methane concentrations to aquifer type and to other water-quality constituents;

(2) Soil-gas-methane concentrations measured at ground-water sites, gas seeps, and gas wells;

(3) Comparison of the molecular and isotopic composition of gases in ground water, soil, gas-well surface casings, and cathodic-protection wells to the composition of formation gases; and

(4) Gas-well construction and remediation records, a geologic conceptualization of diffusion and fracture-formation processes, relation of dissolved-methane concentrations to mapped geologic fractures, and a physical conceptualization of gas flow in the subsurface environment.

Data used in this investigation were collected primarily by the U.S. Geological Survey from August 1990 through May 1991 and consist of: (1) Location and construction of sampled water wells and gas wells, (2) dissolved-methane concentrations and other water-quality determinations from domestic wells in or adjacent to the Animas River valley, (3) concentrations of methane in soil gas near water wells and adjacent to gas-well casings within about 0.5 mi of the Animas River valley; and (4) molecular and methane-isotope compositions for selected gas samples collected from ground water, soil, and gas wells. These data are compiled in a separate report (Chafin and others, 1993).

## General Description of Study Area

The study area (fig. 1) is along the Animas River valley in the San Juan Basin between about 3 mi south of Durango, Colorado, and Aztec, New Mexico. The valley generally is 1 to 1.5 mi wide except for a section along the Colorado-New Mexico State line, where the valley is as narrow as 0.2 mi. The elevation of the Animas River decreases from about 6,500 ft at Durango to about 5,600 ft at Aztec. North of Cedar Hill, New Mexico (pl. 1), the valley largely consists of a terrace beside a narrow, incised river bottom. South of Cedar Hill, the valley floor slopes gently from the valley walls to the river channel. Between Durango and Cedar Hill, the valley walls generally are several hundred feet high; Mount Nebo, which is located a few miles north of Cedar Hill (pl. 1), peaks about 1,200 ft above the valley. South of Cedar Hill, the valley is bounded by hills that generally are 50 to 150 ft above the valley margin.

The climate of the study area is semiarid. The 1951-80 annual average precipitation at Durango was 18.6 in (National Oceanic and Atmospheric Administration, 1990). Annual precipitation gradually decreases from Durango to Aztec, where the average annual precipitation is 9.33 in. (Stone and others, 1983). Periodic winter storms are not uncommon, especially near Durango.

Land use in the study area is varied. Irrigated agriculture and cattle grazing are widespread throughout the valley. Residences, which consist almost exclusively of single-dwelling houses, generally are several times more dense in the New Mexico part of the study area than in the Colorado part. Housing density ranges from one house on a tract of land that consists of dozens

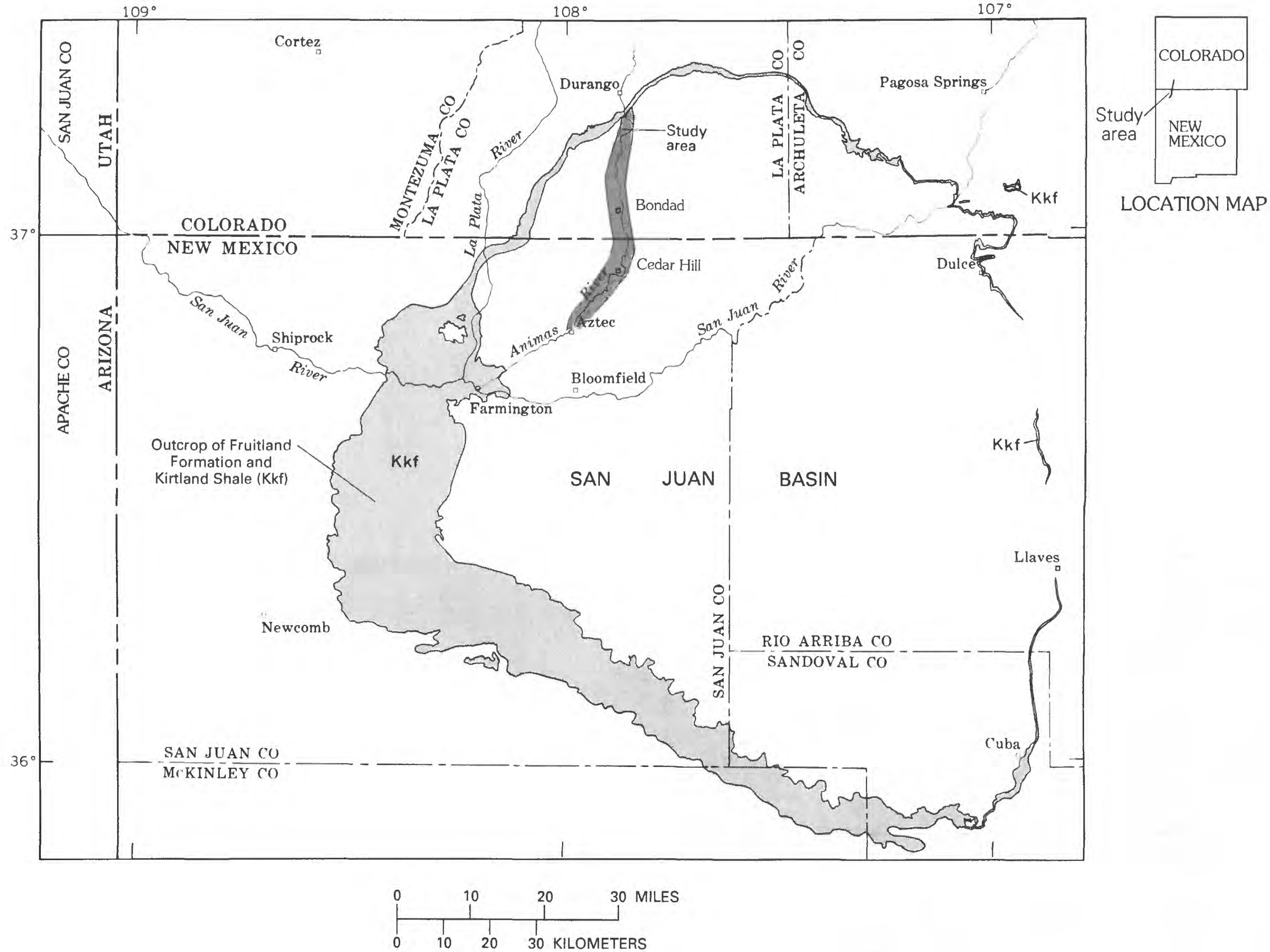



**Figure 1.** Location of the study area in the San Juan Basin (modified from Fassett and Hinds, 1971, p. 2).

of acres to several houses per acre, especially near Aztec. Few services exist in the study area. Three gasoline stations with food stores operate near the Colorado-New Mexico State line. Gas wells, pipelines, and gas-well access roads are located throughout the study area.

### Selected Previous Studies

The presence, origins, and effects of natural gas in ground-water systems has been described and evaluated by several investigators. Water levels of water wells near Houston, Texas, increased during 1942-44 because of a leaking gas well (Rose and Alexander, 1945). Water-level rises of 4 to 61 ft were measured at distances of 1.5 to 11.7 mi from the gas well. Some water wells produced gas with water and, in extreme cases, the ground around casings was eroded by the forceful venting of gas (cratering). The authors concluded that serious damage could be caused to water wells in Houston if gas wells near the city became defective and gas entered water-bearing sands.

Methane in fresh-water aquifers of southwestern Louisiana was studied by Harder and others (1965). They measured methane concentrations in the water as large as 127 mg/L; the largest concentrations were measured in the vicinity of three oil and gas fields. Harder and others (1965) concluded that methane in ground water near these fields may have been provided by leaky or defective casing in existing oil and gas wells. They attributed the presence of methane in other areas to degradation of organic debris within the aquifers. These investigators concluded that dissolved-methane concentrations as small as 1.1 mg/L theoretically can create an explosion hazard in poorly ventilated air spaces contacting flowing water.

Seepage of large quantities of natural gas over an unpopulated area of about 0.9 $mi^2$ in a gas-well field in northwestern Oklahoma was described by Preston (1980). Analyses of seepage and produced gases caused the author to suspect that a faulty gas well caused the seepage.

Carbon isotopes were used to determine sources of methane in several ground-water flow systems, mostly in Canada (Barker and Fritz, 1981a). Two systems in rocks of Quaternary age that do not overlie major sources of *thermogenic gas* contained *biogenic gas*. These investigators studied three ground-water systems potentially underlain by thermogenic natural-gas deposits and concluded a biogenic source for methane in two systems and both biogenic and thermogenic sources in the other.

A biogenic source for methane in near-surface (308 to 400 ft deep) ground water in bedrock in Weld County, Colorado, was concluded on the basis of carbon-isotope data (Rice and Threlkeld, 1982). Rice and others (1984) determined that thermogenic gas was seeping to the surface at LaSalle, Colorado, and believed that deep, abandoned water wells were the conduits for upward, near-surface migration but were not able to conclude whether the gas migrated from the producing formation at about the 7,000 ft depth because of natural phenomena or drilling activities.

The effects of a leaking gas well in Ohio on ground-water chemistry were studied by Kelly and others (1985). They reported that elevated methane concentrations were accompanied by elevated concentrations of iron, manganese, calcium, sulfide, alkalinity, and pH and by decreased concentrations of dissolved oxygen, sulfate, and nitrate. These investigators report that homeowners complained about an intense sulfide odor, increased iron concentrations, and staining of commodes with a black precipitate.

Methane-carbon isotopes were used to study the source of hydrocarbon gases at depths from 78 to 2,000 ft in aquifers in rocks of Eocene age in east-central Texas (Grossman and others, 1989). They determined that these gases originated by bacterial processes.

Gas-composition data from a variety of sources in the Animas River valley between Bondad, Colorado, and a few miles south of Aztec, New Mexico, were reviewed by Shuey (1990). He concluded that about half of the samples from domestic water wells and seeps in fields and the river contained gas from the Fruitland Formation that had migrated up uncemented intervals of *conventional gas wells* after initial dewatering of *coal-bed gas wells* completed in the Fruitland Formation.

Gases in ground water, from a surface seep, from *cathodic-protection wells*, and from gas-well *surface casings* in the Cedar Hill, New Mexico, area were studied by Beckstrom and Boyer (1991). They could not determine the specific sources of gases in ground water and determined that the surface-seep gas was thermogenic gas from an unspecified source. Beckstrom and Boyer (1991) determined that the gas in three surface casings migrated from the Fruitland Formation and moved up *annuli* of conventional gas wells that were not cemented across coals of the Fruitland Formation.

Oldaker (1991) summarized the hydrogeology of the Animas River valley. This study included a history of gas development and water-quality issues in the study area based on published accounts and personal interviews. These sources indicate gas and oil seeps in southeastern Utah and in the areas bordering the San Juan Basin. However, no known gas seeps or methane-affected ground water were reported along the Animas River valley between Durango, Colorado, and Aztec, New Mexico, prior to local gas-well drilling. The author concluded that the sources of organic gases could be natural or could be caused by human activities but that the available data were inconclusive.

Fractures were mapped between Bondad and a few miles south of Cedar Hill and fractures were correlated with water wells containing methane (Steven T. Finch, John W. Shomaker, Inc., written commun., 1992). The results indicated a weak, negative correlation between fracture density and the number of water wells containing methane and relatively strong, positive correlations between (1) the numbers of gas wells and water wells containing methane; and (2) the numbers of structural folds and water wells containing methane.

## History of Gas Development

The history of conventional gas development in the vicinity of the study area is summarized by Matheny and Ulrich (1983). Shortly after 1900, a commercially unsuccessful gas well was drilled to a depth of 350 ft in the Farmington Sandstone Member of the Kirtland Shale at Farmington, New Mexico (fig. 1). In 1921, the first commercial gas well in the San Juan Basin was drilled into the Farmington Sandstone Member 1 mi south of Aztec. Exploration activities slowed in the 1930's but increased during the 1940's after discovery of gas in the Pictured Cliffs Sandstone in 1941. By 1949, additional discoveries of gas in the Dakota Sandstone, Pictured Cliffs Sandstone, and the Mesaverde Group indicated that the San Juan Basin might have substantial gas-producing capacity, especially from the Mesaverde Group over much of the study area.

There was a period of boom in the San Juan Basin from 1950 to 1953 (Matheny and Ulrich, 1983). In 1950, additional gas-bearing zones were discovered in the Fruitland Formation, Mesaverde Group, and the Dakota Sandstone in Colorado. The completion of a natural-gas transmission line from the San Juan Basin to the west coast of the United States in 1951 greatly enhanced development, and substantial accumulations of gas were discovered in 1952, especially in the Mesaverde Group. Development and exploration continued at a more moderate pace during 1954-75 when most conventional gas wells were completed in the study area. The rate of development escalated during 1976-81 after the New Mexico Oil and Gas Commission authorized the drilling of a second well in the Mesaverde Group in each 320-acre producing unit in 1975 and the completion of additional wells in the Dakota Sandstone in 1980. The Colorado Oil and Gas Commission authorized the completion of additional wells in the Mesaverde Group and Pictured Cliffs Sandstone in 1979. These authorizations quickened the development rate, which was greatly enhanced by the 1976 issuance of a sharp price increase for interstate gas sales by the Federal Power Commission. Conventional completions decreased after 1981 because of the nationwide surplus of natural gas.

Intensive development of methane from coal beds of the Fruitland Formation began in the mid-1980's in response to tax credits authorized by the Crude Oil Windfall Profits Tax Act of 1980. Originally scheduled to last through 1990, those credits were extended through 1992. Coals in the Fruitland Formation in the Cedar Hill area were the first to be studied and developed. The Gas Research Institute (1991, p. 6) estimated that, at the end of 1990, about 1,000 coal-bed-methane wells in the Fruitland Formation had a cumulative production of about 100 billion $ft^3$ of gas, primarily in the north-central part of the basin.

Locations of gas wells in and near the study area are shown on plate 1. About 165 gas wells completed in the Mesaverde Group (121 in New Mexico and 44 in Colorado) are within an area extending out about 0.5 mi from the Animas River valley in the study area; these wells were completed from 1951 to 1988. In the same area, wells in the Pictured Cliffs Sandstone number about 78 (75 in New Mexico and 3 in Colorado and were completed from 1951 to 1986. Wells in the Dakota Sandstone number about 42 (27 in Colorado and 15 in New Mexico) and were completed from 1959 to 1990. About 30 coal-bed wells were completed in the Fruitland Formation within about 0.5 mi of the Animas River valley in the New Mexico part of the study area from 1972 to 1990. About the same number were completed in the Colorado part of the study area from 1986 to 1990.

## Acknowledgments

The U.S. Geological Survey and the author thank homeowners in the study area for allowing sampling of their wells and for providing other useful information. We also thank gas producers for access to gas-well sites and for contributing information. Gratitude is extended to the Aztec District of the NMOCD for direct assistance, a large volume of data, and valuable technical advice. The author also is indebted to Dudley Rice, Charles Threlkeld, and Augusta Warden (U.S. Geolog-

ical Survey, Geologic Division) for valuable technical assistance, timely analysis of gas samples, and insightful reviews of manuscripts.

## GEOLOGY OF THE STUDY AREA

The study area is located on the northwestern side of the San Juan Basin (fig. 1), which is a structural basin of Laramide origin. Geologic structural elements surrounding the San Juan Basin are shown in figure 2. The major element bounding the study area to the north and west is the Hogback Monocline, which crosses the Animas River valley about 3 mi south of Durango. The San Juan Uplift, which is adjacent to the basin to the north and northeast of Durango, forms the highest uplift around the basin. The internal structure of the basin is illustrated by the contour map of the top of the Huerfanito Bentonite Bed of the Lewis Shale (fig. 3), which was deposited before major uplift had occurred around the basin (Fassett and Hinds, 1971, p. 34). The basin is asymmetric and has steeply dipping beds around the northwestern, northern, and northeastern rim of the basin and gentle, northeastward dips in the southwestern and southern parts of the basin. The deepest part of the basin is along a northwest-trending axis that crosses the study area near the Colorado-New Mexico State line. Precambrian crystalline rocks are more than 14,000 ft beneath the land surface in the deepest part of the basin (Laubach and Tremain, 1991, p. 3). Structures in the San Juan Basin consist of minor anticlinal and synclinal noses superimposed on regional homoclinal dips; these folds have structural relief of less than 200 ft (Laubach and Tremain, 1991, p. 3). Decker and others (1988, p. 225) show structural relief on the Pictured Cliffs Sandstone in the Cedar Hill area to be about 20 to 40 ft. These authors state that structural highs and lows may be related to faulting rather than folding. Ambrose and Ayers (1991, p.50) show fault offsets of about 40 ft in formations of late Cretaceous age beneath Cedar Hill, New Mexico.

Surface evidence of faulting in the study area is sparse, partly because of poor outcrop exposure, especially north of Bondad and on the western side of the valley south of Bondad. Long segments of exposed outcrops show little or no faulting. Most observed faults are in the Bondad area. Faults showing offsets of about 70, 65, and 15 ft were observed there. Another fault with about 50 ft of offset was observed a few miles north of Aztec.

Sediments of Cambrian through Quaternary age fill the San Juan Basin. Because the oldest formations from which gas is produced beneath the study area are of Cretaceous age, only sediments of Cretaceous and younger age are described in this report (fig. 4).

### Dakota Sandstone

The Dakota Sandstone is the oldest formation of Cretaceous age in the basin and is the oldest formation in the basin from which substantial quantities of gas are produced. Kelso and others (1980, p. 3) describe the Dakota Sandstone according to three intervals. The lowest interval consists of a coarse, fluvial conglomerate. The middle interval consists of a carbonaceous shale and coal sequence with interbedded fluvial sandstones. The upper interval consists of a fine-grained marine sandstone. Gas-well-drilling data indicate that the thickness of the Dakota Sandstone ranges from about 180 to 300 ft beneath the study area. Within about a mile of the Hogback Monocline, the top of this unit plunges to a depth of about 6,900 ft beneath the Animas River, gradually deepens dipward to a maximum depth of about 7,200 ft at the basin hinge line near the State line, and rises to a depth of about 6,700 ft at Aztec because of the northward dip toward the hinge line.

### Mancos Shale

Brogden and Giles (1976) describe the Mancos Shale near Durango as a dark gray, silty and sandy marine shale with interbedded sandstones and limestones. Gas-well-drilling data indicate that the thickness of the Mancos Shale ranges from about 1,800 to 2,200 ft beneath the study area. This unit is not exposed south of the Hogback Monocline near Durango.

### Mesaverde Group

Members of the Mesaverde Group yield the most important volumes of conventional (non-coal-bed) gas in the study area. The Mesaverde Group consists of three formations: the basal Point Lookout Sandstone, the Menefee Formation, and the Cliff House Sandstone.

Gas-well-drilling data indicate that the total thickness of the Mesaverde Group ranges from about 500 to 1,150 ft beneath the study area but generally is 800 to 1,000 ft thick. The formations of the Mesaverde Group do not crop out south of the Hogback Monocline. Depths to the top of the Mesaverde Group beneath the Animas River increase from about 4,300 ft near the Hogback Monocline to a maximum of about 4,600 ft near the State line and decrease to about 4,000 ft at Aztec. Craigg and others (1990) describe the Point Lookout Sandstone as a sequence of light-

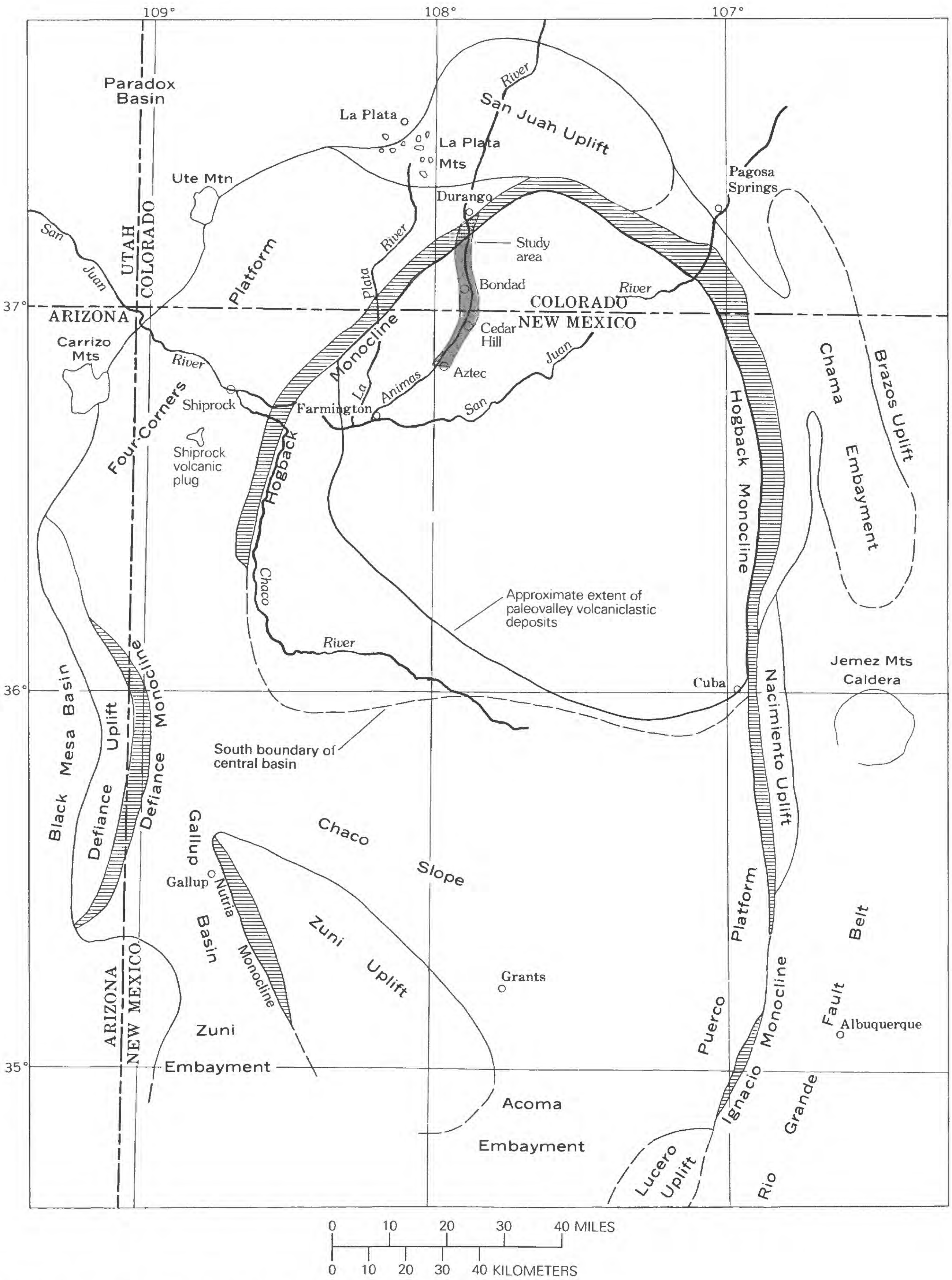



**Figure 2.** Structure of the San Juan Basin (modified from Kelley, 1951, p. 125).

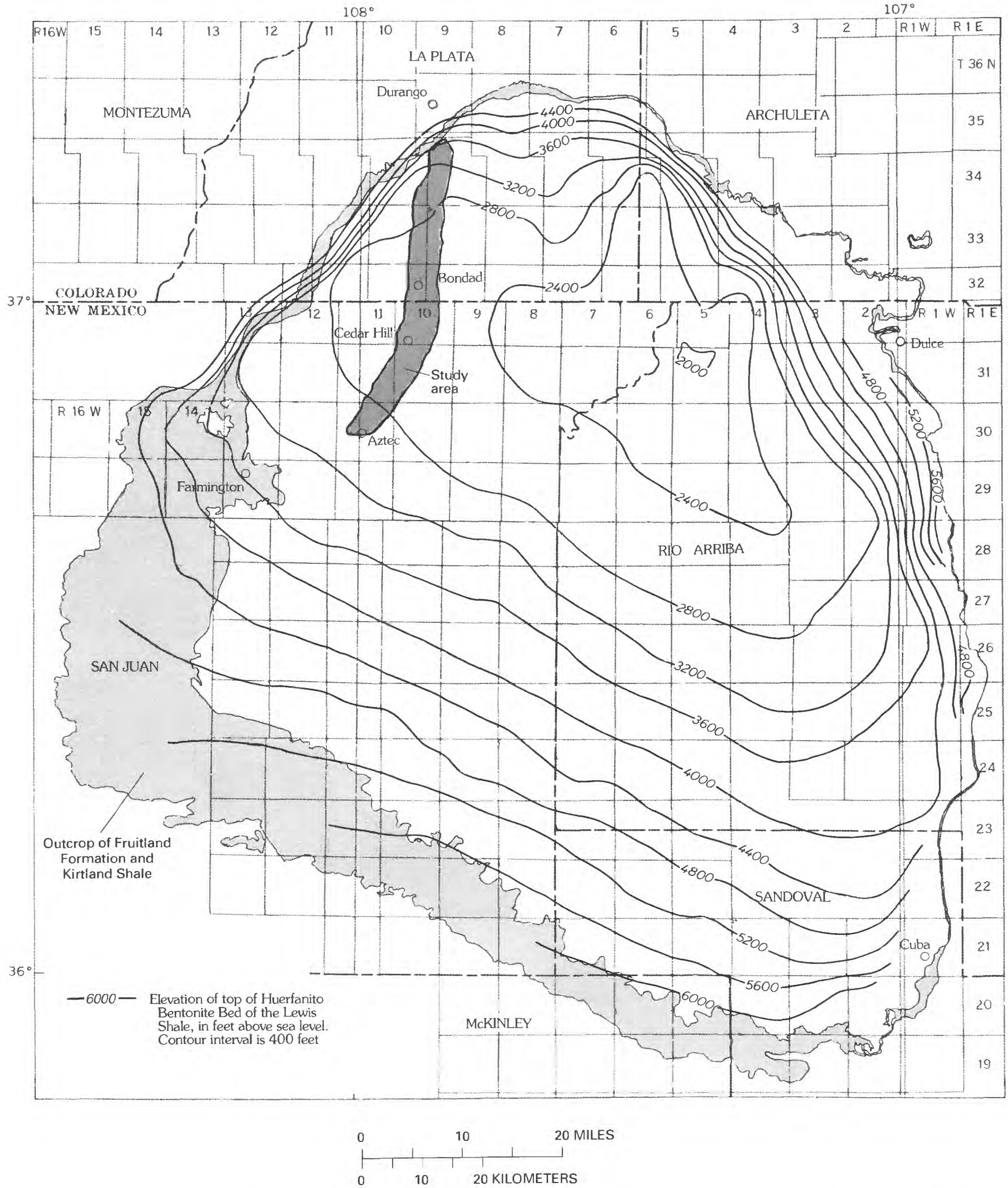



**Figure 3.** Structure contours of the Huerfanito Bentonite Bed of the Lewis Shale (modified from Fassett and Hinds, 1971, p. 36).

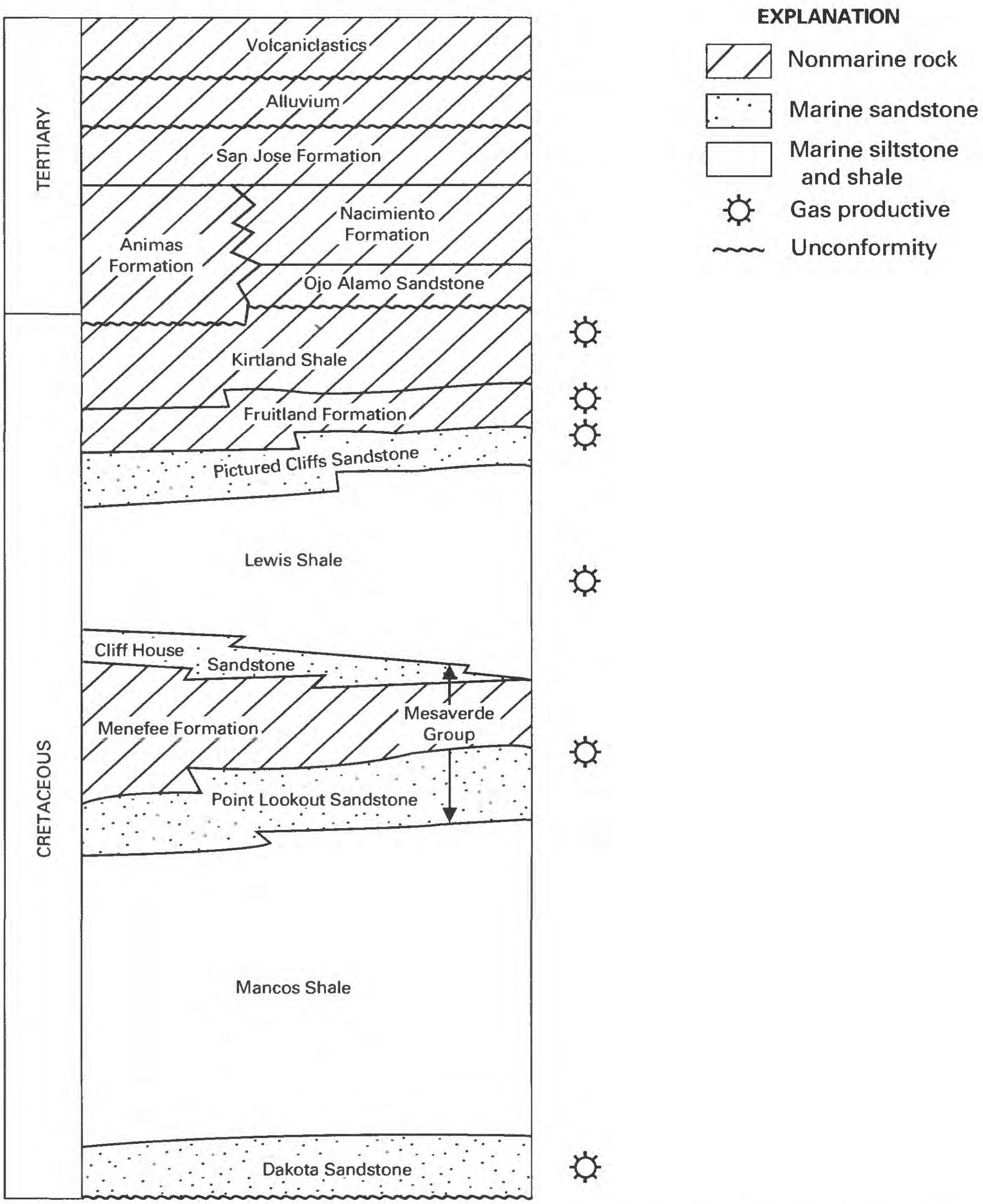



**Figure 4.** Sediments of Cretaceous and younger age in the vicinity of the study area (modified from Rice and Threlkeld, 1988, p. 8).

gray, thick- to very thick-bedded, very fine- to medium-grained marine sandstone. Gas-well-drilling data indicate that the Point Lookout Sandstone is 80 to 300 ft thick beneath the study area but generally is 100 to 200 ft thick.

Levings and others (1990a) describe the Menefee Formation as interbedded and repetitive sequences of differing thicknesses of fluvial and swamp deposits of sandstone, siltstone, shale, claystone, carbonaceous shale, and coal. Gas-well-drilling data indicate that the Menefee Formation is 100 to 650 ft thick (with greater thicknesses to the south) but generally is 300 to 400 ft thick.

Thorn and others (1990) describe the Cliff House Sandstone as generally consisting of thick- to very thick-bedded marine sandstone, which commonly has interbeds of gray shale and silty shale. Gas-well-drilling data indicate that this formation is 50 to 500 ft thick beneath the study area but generally is 100 to 200 ft thick.

### Lewis Shale

Kelso and others (1980, p. 7) describe the Lewis Shale as a dark gray, gray-green and black marine shale with sandy intervals, calcareous concretions, and numerous bentonite beds, the most prominent of which is the Huerfanito Bentonite Bed. Gas-well-drilling data indicate that the Lewis Shale is 1,300 to 1,900 ft thick beneath the study area but generally is 1,500 to 1,700 ft thick. One well produces gas from the Lewis Shale beneath the study area at Bondad. This well was completed in fractured siltstones and silty shales near the base of the formation at a depth of about 4,100 ft in 1969.

### Pictured Cliffs Sandstone

The Pictured Cliffs Sandstone is a gas-producing formation in the southern half of the study area. This formation is described by Dam and others (1990) as generally consisting of an upward-coarsening sequence of very fine- to medium-grained marine sandstone with thin interbeds of dark shale, especially in the lower part of the unit. Gas-well-drilling data indicate that the thickness of the Pictured Cliffs Sandstone ranges from 70 to 350 ft beneath the study area but generally is 100 to 250 ft thick. Depths to the top of the Pictured Cliffs Sandstone beneath the Animas River increase from about 2,400 ft near the Hogback Monocline to a maximum of about 2,700 ft near the State line and decrease to about 2,100 ft at Aztec.

### Fruitland Formation

The coals of the Fruitland Formation, the uppermost formation that bears substantial quantities of commercial gas in the San Juan Basin, recently have begun to produce more natural gas than all of the deeper, conventional gas-producing formations combined (Frank Chavez, NMOCD, oral commun., 1991). Fassett and Hinds (1971, p. 17) describe the Fruitland Formation as interbedded fluvial sandstone, siltstone, shale, carbonaceous shale, carbonaceous sandstone and siltstone, and swamp coals. The coal beds are discontinuous, generally pinching out within a few hundreds of feet, except for some beds that are traceable for several miles. These authors also describe a general vertical succession: thicker coal beds invariably are confined to the lower one-fifth to one-third of the formation; sandstone generally is more abundant in the lower part than the upper part; and siltstone and shale predominantly are in the upper part. Gas-well-drilling data indicate that the thickness of the Fruitland Formation beneath the study area ranges from about 250 to 750 ft but generally is 300 to 400 ft in New Mexico and 400 to 500 ft in Colorado. An isopach map by Fassett and Hinds (1971, p. 53) indicates that the total coal thicknesses of the Fruitland Formation beneath the study area probably are about 30 to 70 ft; the greatest thicknesses are near the State line and generally thin to the north and south. However, thicknesses of individual coal beds range from that of small stringers to about 33 ft, as determined from a map of the thickest individual coal units (Fassett and Hinds, 1971, p. 55). Depths to the top of the Fruitland Formation beneath the Animas River increase from about 1,800 ft near the Hogback Monocline to a maximum of about 2,200 ft near the State line and decrease to about 1,800 ft at Aztec.

### Kirtland Shale

The fluvial Kirtland Shale is described by Fassett and Hinds (1971, p. 24). A lower shale section is overlain by the Farmington Sandstone Member and an upper shale section. Gas-well-drilling data indicate that the thickness of the Kirtland Shale beneath the study area generally is 900 to 1,200 ft.

### Ojo Alamo Sandstone

The Ojo Alamo Sandstone, the oldest formation of fully Tertiary age in the study area, is described by Fassett and Hinds (1971, p. 28) as massive arkosic sandstone and conglomeratic sandstone interbedded with shale. A subsurface-extent map by Fassett and Hinds (1971, p. 20) indicates that the Ojo Alamo Sandstone is not present beneath this study area northward of a line a few miles north of the State line. Gas-well-drilling data indicate that the thickness of the Ojo Alamo Sandstone beneath the study area ranges from 40 to 200 ft but generally is 70 to 150 ft.

## Animas and Nacimiento Formations

The Animas and Nacimiento Formations constitute most of the fill of Tertiary age in the San Juan Basin and extend beneath the entire study area. These formations are important sources of ground water in the Animas River valley, especially north of Cedar Hill. The Animas Formation consists of the McDermott Member of latest Cretaceous age and a much thicker, unnamed member of Paleocene age. The McDermott Member is described by Brogden and Giles (1976) as coarse, tuffaceous sandstone and thick beds of fine- to coarse-grained tuff with interbedded shale, breccia, and volcanic conglomerate. Where this member is exposed at the Hogback Monocline south of Durango, it is about 127 ft thick (Stone and others, 1983, p. 30). The McDermott Member probably extends only a few miles south into the study area. Fassett (1974, p. 229) describes the unnamed member of the Animas Formation as varicolored and interbedded tuffaceous sandstone, conglomerate, and shale. The Animas Formation grades basinward into the Nacimiento Formation, but because of the complex interfingering within and between these formations and the similarity of their lithologies, geologists do not agree on the locations of the contact between them. Tweto (1979) reports that the contact crosses the Animas River valley near the middle of the Colorado reach of the study area.

Brown and Stone (1979) describe the Nacimiento Formation as claystone, shale, siltstone, and coarse, conglomeratic, massive sandstone. The drillers' log for Bryce 1 (from COGCC records), a well drilled in Bondad at 33N-09W-31CCD (see "System of Numbering Wells" following the "Glossary"), indicates that the Nacimiento Formation is about 85 percent shale. In the upper 900 ft, shale layers had thicknesses that ranged from 7 to 152 ft and averaged 47 ft. Shale thicknesses of 106 and 138 ft also were logged. Sandstone thicknesses ranged from 3 to 45 ft and averaged 9 ft. Brimhall (1973, p. 201) indicates that most sandstones of the Nacimiento Formation extend laterally only a few thousand feet.

The Animas and Nacimiento Formations are on the Kirtland Shale in the northern part of the study area where the Ojo Alamo Sandstone is missing. Gas-well-drilling data indicate that beneath the Animas River, depths to the base of the Animas and Nacimiento Formations are about 900 ft near the Hogback Monocline, gradually increase to about 1,000 ft near the State line, and gradually decrease to about 700 ft at Aztec. These depths can be taken as the thicknesses of the Animas and Nacimiento Formations beneath the valley, except for additions (generally less than 100 ft) for higher topography.

## San Jose Formation

The San Jose Formation is present only in the New Mexico and southernmost few miles of the Colorado parts of the study area. Levings and others (1990b) describe the San Jose Formation as interbedded fluvial sandstone, siltstone, and variegated shale of Eocene age. The contact between the underlying Nacimiento Formation and the San Jose Formation generally is 200 ft or more above the valley floor.

## Alluvium of Middle Tertiary Age

The presence of paleovalley volcaniclastic deposits of Oligocene age (discussed in the following subsection "Volcaniclastic Deposits of Oligocene Age") stratigraphically higher than that of the lower alluvial terrace of the Animas River valley in the study area indicates that this and older terraces are of late Eocene or earliest Oligocene age and have been exhumed during Quaternary times. Terrace sequences in the northern San Juan Basin represent several million years of tectonically induced erosional cycles between the final deposition of the San Jose Formation in middle Eocene times and valley infilling with volcanic material of early Oligocene age. Terrace deposits in the northern San Juan Basin are approximately equivalent in age to the Telluride Conglomerate in the San Juan Mountains north of Durango. This formation is overlain by basal volcanic deposits of early Oligocene age (Epis and Chapin, 1975, p. 65; Tweto, 1979).

The lower Animas River valley is formed by a discontinuous terrace between Durango and Cedar Hill. The same river-cut surface can be traced to Aztec, although it is buried with deep gravel and sand, unlike the cobbly sections at and north of Cedar Hill. Bondad, Sunnyside Mesa, and Cedar Hill lie on relatively well preserved segments of this terrace, which is about 1 mi wide at these and other locations.

Well logs (Colorado and New Mexico State Engineer records) indicate that most terrace deposits at and north of Cedar Hill are boulders and cobble, some-times overlying thinner layers of sand and gravel. South of Cedar Hill, more gravel and sand are present. Generally, terrace deposits are 25 to 50 ft deep, with greater depths resulting from higher land-surface elevations near valley walls and from channelizing into bedrock. South of Cedar Hill, alluvial deposits generally are 30 to 40 ft thick near the river, but locally thicknesses increase to about 100 ft along the higher valley margins.

## Volcaniclastic Deposits of Oligocene Age

Volcaniclastic rocks deposited in paleovalleys were discovered during this study. Outcrops of these deposits were observed in and near the study area and other scattered locations throughout the northern San Juan Basin (fig. 2). These rocks consist of banded grey, maroon, and tan outcrops that generally are sparse and discontinuous and locally mask sandstone and shale layers of the Animas, Nacimiento (fig. 5), and San Jose Formations (fig. 6). The areal extent of these deposits, which should be considered to be minimum, is approximately delineated by the Hogback Monocline and the distal outcrop of the Nacimiento Formation.

Near Cedar Hill, in the northwestern quarter of 31N-10W-06, volcaniclastic rocks were observed about 20 ft above the Animas River at an elevation of about 5,800 ft. At the foot of Mt. Nebo, about 1 mi north of Cedar Hill, these rocks are directly above the lower Animas River valley, stratigraphically higher than the lower terrace alluvium (fig. 7). About 0.5 mi northwest of Cedar Hill, in the southeastern quarter of 32N-10W-27, these rocks are visible as an isolated outcrop on the southern side of Mt. Nebo at an elevation of about 6,500 ft (fig. 7). About 3.5 mi east of Bondad, a large outcrop of these sediments (fig. 6) ranges in elevation from about 6,750 to 7,250 ft along the northern flank of the Mesa Mountains, which are formed from the San Jose Formation. This outcrop projects above Florida Mesa, suggesting that Florida Mesa was once covered by this volcaniclastic unit. This conclusion is supported by the occurrence of tuffaceous sand on the cobble and gravels of the upper terrace of this mesa (Moore and Gillam, 1984, p. 204). Volcaniclastic rocks were observed at elevations near 8,000 ft along the north and 7,600 ft along the eastern margins of the San Juan Basin.

Outcrops of the volcaniclastic rocks give the appearance of mudstone and shale, weathering into badlands topography. Freshly exposed deposits at 31N-11W-14 about 5 mi southwest of Cedar Hill (at an elevation of about 5,860 ft) consisted of a dense, dark, glassy material that, when dry, developed a mottled purple-green color. Another sample collected from a roadcut at 32N-09W-27 about 4 mi east of Bondad (elevation about 6,700 ft) had a similar appearance. X-ray-diffraction analysis indicates similar compositions for both samples, with the following constituents listed in order of decreasing relative abundance:

| 31N-11W-14 | 32N-09W-27 |
|---|---|
| Quartz | Quartz |
| Amorphous material | Amorphous material |
| Kaolinite | Kaolinite |
| Potassium feldspar | Smectite |
| Hematite | Mica |
| Mixed-layer clays | Mixed-layer clays |
| Mica | Pyroxene |
| Pyroxene | Anatase |

Scanning-electron-microscope spectral analysis indicates the following selected oxide compositions (in percent):

| | 31N-11W-14 | 32N-09W-27 |
|---|---|---|
| $SiO_2$ | 66.68 | 71.75 |
| $Al_2O_3$ | 21.45 | 17.80 |
| $TiO_2$ | 0.73 | 0.93 |

The presence of abundant amorphous material, indicating glass, and the infilling of terrain by these rocks over a large elevation range indicate that these rocks are derived from volcanic activity, probably mostly water-transported volcaniclastics, but possibly with some air-borne volcanic ash. The clay minerals probably formed by weathering and diagenesis during burial of the glass-rich sediments.

These volcaniclastic rocks are considered to be Oligocene in age. These rocks cannot be older than middle Eocene age because they buried terrain cut deeply in the San Jose Formation of early to middle Eocene age. At least several old-age erosional cycles occurred between final deposition of the San Jose Formation and initial deposition of these volcaniclastic rocks. The age of the Shiprock volcanic plug (fig. 2), which Laughlin and others (1986, p. 365) dated by K-Ar at about 26.4 million years (late Oligocene age) suggests an Oligocene age for the volcaniclastic rocks. This plug is about 10 mi southwest of the San Juan River at Shiprock, New Mexico, and extends about 2,200 ft higher than the river. Because terraces of the San Juan River valley are continuous with terraces of

**Figure 5.** Paleovalley, volcaniclastic mudstones (upper right) masking sandstones of the upper Nacimiento Formation. Location is at 31N-11W-14, about 5 miles southwest of Cedar Hill, New Mexico. Elevation is about 5,900 feet. View looking northeast.

the Animas River valley (Gillam and others, 1984, p. 163) and the Chaco River drainage to the south of the Shiprock plug (Watson and Wright, 1963, p. 538), the presence of volcaniclastic rocks in the Animas River drainage indicates that the plain surrounding the Shiprock plug can be assumed to closely represent the prevolcanic erosional surface and that thick volcaniclastic deposits were already deposited in the San Juan Basin when the Shiprock plug was intruded. This conclusion is consistent with the history of the San Juan volcanic field north and northeast of the San Juan Basin, as reported by Lipman and others (1978). Eruption of voluminous intermediate-composition lavas and breccias began from widely scattered volcanoes between about 35 and 30 million years ago (early to middle Oligocene age). Between about 30 and 26.5 million years ago (middle to late Oligocene age), at least 16 major ash-flow sheets formed a great welded-tuff plateau overlying the more intermediate-composition lavas and breccias. These ash-flow sheets were about half as voluminous as the older intermediate-composition lavas. Much smaller volumes of volcanic material were extruded from about 22.5 to 4 million years ago (Miocene to late Pliocene age). The history of the San Juan volcanic field implies that major volcaniclastic deposition in the northern San Juan Basin began early in the Oligocene Epoch. Other investigators (Steven, 1975; Bond, 1984; Laubach and Tremain, 1991) inferred a cover of volcaniclastic debris of Oligocene age over the northern San Juan Basin, although they assumed that all evidence of this debris has been eroded away.

These volcaniclastic rocks allow more accurate age dating of the landforms, alluvial terrace deposits, and exposed faults in and near the study area. These rocks also allow a more accurate estimate of the maximum burial depths and burial history of gas-yielding formations beneath the study area. The age of the landforms and alluvial terrace deposits in the study area were discussed in the preceding subsection. The burial history of gas-yielding formations is discussed in the subsection "Indigenous Gas in the Animas and Nacimiento Formations." The age of exposed faults in

**Figure 6.** Outcrop of paleovalley, volcaniclastic mudstones flanking north side of the Mesa Mountains, which are formed from the San Jose Formation. Location is at 32N-09W-27, about 3.5 miles east of Bondad, Colorado. Elevation of outcrop ranges from about 6,750 to 7,250 feet. View looking east.

the study area is discussed in the subsection "Natural Fractures."

### Alluvium of Quaternary (?) Age

The Animas River has incised the terrace that constitutes most of the lower valley, probably during latest Pleistocene and Holocene times (but possibly prior to burial by volcaniclastic sediments of Oligocene age). Incision into bedrock decreases from about 70 ft at Durango to none at Cedar Hill. At and south of Cedar Hill, exposed bedrock is not evident beneath terrace deposits along the course of the river. At various locations along the river, small, active floodplains have developed and have been filled with alluvium of Quaternary (?) age consisting of gravel, sand, and clay. Because these areas are prone to flooding, they generally are not inhabited.

## GROUND WATER IN THE STUDY AREA

Ground water in the study area is produced from two major sources: alluvium and bedrock. Bedrock wells are the most common well type north of Cedar Hill, where flood-plain deposits are limited in extent and where terrace deposits are not dependable sources of water. At and south of Cedar Hill, alluvial sources of water are more dependable, and bedrock wells are rare in the Animas River valley.

### Alluvium

Alluvial wells produce from terrace and flood-plain deposits. Terrace deposits of middle Tertiary age were deposited on an abandoned flood plain above the current level of the river and thus cannot be recharged by it. Most of the Animas River valley in the study area consists of a single terrace that can be traced from the Hogback Monocline to Cedar Hill and that has been dissected by river downcutting. Florida Mesa is a


**Figure 7.** Paleovalley, volcaniclastic mudstones (directly above lower valley) stratigraphically higher than the lower terrace alluvium of the Animas River valley. Location is about 1 mile north of Cedar Hill, New Mexico. Note location of isolated outcrop of volcaniclastic mudstones lying on the San Jose Formation at right skyline at an elevation of about 6,500 feet. View looking east.

much larger, older terraced plain bounding the Animas River valley along the eastern side of most of the Colorado reach of the study area.

The bottom of terrace deposits varies in depth according to whether the bedrock was deeply channelized by the ancient river and tributaries or was less deeply channelized or was in overbank areas. Wells drilled deeply enough into old channels generally are dependable sources of water, whereas wells drilled into these other areas are not. Reported depths of wells in terrace deposits (Chafin and others, 1993) ranged from 20 to 140 ft; however, only one well exceeded 80 ft in depth, and most of the deeper wells probably were drilled into bedrock for storage capacity. Measured depths to water ranged from 3 to 48 ft.

Recharge to terrace deposits is from infiltration of local precipitation, intermittent runoff from tributary arroyos, spring and diverted ditch water, and discharge from bedrock. Several large springs along the western edge of Florida Mesa discharge terrace-deposit water down the valley walls, and this water subsequently recharges terrace deposits in the Animas River valley several hundred feet lower. Terrace-deposit water generally flows in a downvalley direction, and local flow directions follow ancient channels. Where substantial thicknesses of terrace deposits are saturated, they provide wells with large yields.

South of Cedar Hill, the valley probably is filled with flood-plain (valley-fill) sediments that are hydraulically connected to the river. These sediments rest on the same river-cut bench as do the terrace deposits north of Cedar Hill. South of Cedar Hill, however, the gradient of the river decreases south of the basin hingeline, and bedrock is not exposed along the river. North of Cedar Hill, flood-plain deposits are in relatively small, isolated areas between greater terraced areas. North of Cedar Hill, only 3 wells in flood-plain deposits were sampled, whereas at and south of Cedar Hill, all but 6 of 117 wells sampled were considered to be flood-plain-deposit wells. Alluvial wells at Cedar Hill probably are hydraulically connected to the river and, therefore, the aquifer was reported as valley fill (Chafin and others, 1993). Water-well logs (New Mexico State Engineer records) indicate that south of Cedar Hill the flood-plain alluvium generally is 30 to 40 ft thick near the river but increases to thicknesses of about 100 ft along the higher valley margins. Measured depths to water ranged from about 2 to 48 ft, and the mean depth was 15 ft; greater values were near valley margins. The large grain sizes of the water-yielding layers provide large well yields ranging from about 5 to 50 gal/min; most yields are in the 10- to 20-gal/min range.

Recharge to flood-plain deposits comes from the same sources as recharge to terrace-deposit wells, except that flood-plain deposits also are capable of receiving direct recharge from the Animas River where hydraulic conditions permit. The primary direction of ground-water flow in flood-plain deposits is downvalley. Local flow directions may be modified by tributary ground-water and ditch-infiltration recharge, ground-water withdrawals, and the grain size of sediments in the saturated zone; the greatest flow velocities usually are along coarser river-channel deposits.

### Bedrock

Bedrock wells are completed in the Animas Formation in about the northern one-half of the Colorado reach of the study area and in the Nacimiento Formation south of there. Depths of sampled bedrock wells range from 25 to 380 ft, the greatest depths generally being near valley walls; the median depth is 127 ft. Measured depths to water ranged from 12 to 170 ft (with greatest depths near valley walls), and the median depth was 33 ft. Well yields generally range from 1 to 10 gal/min but typically are 2 to 5 gal/min.

Recharge to the Animas and Nacimiento Formations is from infiltration of precipitation and streamflow on outcrops and from upward migration of water from underlying units (Levings and others, 1990b). Locally and especially for shallower sandstones, ground-water-flow directions are determined by regional topography and geomorphology, with water moving from upland recharge areas to discharge areas along the floors of the Animas River valley and tributary valleys (Stone and others, 1983, p. 44). Because of complex interfingering of shales, siltstones, and sandstones, sandstone aquifers usually extend laterally only a few thousand feet, especially in the Nacimiento Formation, which consists of greater percentages of shale than does the Animas Formation. Discontinuous sandstone aquifers that are not exposed at the land surface probably are recharged at small rates.

## METHANE IN GROUND WATER

Concentrations of dissolved methane, specific conductance, pH, and temperature were measured at 205 ground-water sites (137 alluvial, 68 bedrock) in the study area. The presence or absence of hydrogen sulfide in ground water was determined at each site by a simple smell test. Ground-water sites consisted of 203 wells and two springs. In addition, at 69 of these sites (generally where ground water had substantial concentrations of methane), alkalinity was measured and samples were collected for laboratory determination of concentrations of major ions, bromide, silica, iron, and manganese. These data were collected from August to November 1990 (Chafin and others, 1993). The distribution of dissolved-methane concentrations measured at ground-water sites in the study area is shown on plate 2. This section provides a statistical overview of dissolved-methane concentrations and relates these concentrations to: (1) aquifer type, and (2) concentrations of other water-quality constituents. In addition, this section describes the effects of seasonal hydrologic conditions on methane concentrations in selected wells in the Cedar Hill area.

Most measured methane concentrations in ground water in the study area during August-November 1990 were less than the reporting limit of 0.005 mg/L (table 1). At 70 of 205 sites (34 percent), concentrations equalled or exceeded the reporting limit. Twenty-five sites (12 percent) had concentrations equaling or exceeding 1.0 mg/L, and nine sites (4 percent) had concentrations equaling or exceeding 10 mg/L. The maximum concentration was 39 mg/L. The mean concentration for all 205 sites was 1.3 mg/L.

### Relation to Aquifer Type

To determine the relation of dissolved-methane concentrations to aquifer type, sites were categorized as either alluvial or bedrock. Terrace-deposit sites were grouped with valley-fill sites to define the alluvial-site category because of their hydrologic similarities—unconfined conditions, rapid flow in relatively permeable material, and relatively shallow depths. Bedrock sites included those yielding water from the Animas and Nacimiento Formations. Bedrock wells generally yield water from semi-confined to confined strata that are less permeable than alluvium and are deeper than alluvial wells.

Water from bedrock sites had greater mean and median methane concentrations than water from alluvial sites. Only 23 percent of alluvial sites had detectable methane whereas 57 percent of bedrock sites had

**Table 1.** Summary statistics for dissolved-methane concentrations

[N, number of sites; $Q_{.25}$ (for example), quantile with subscripted number showing fraction of samples with concentration less than or equal to concentration shown; <, less than; $H_2S$, hydrogen sulfide]

| Category | N | Mean | Concentration of methane, in milligrams per liter — Quantiles $Q_{.25}$ | $Q_{.50}$ | $Q_{.75}$ | $Q_{.95}$ | Maximum | Percent of samples equaling or exceeding concentration, in milligrams per liter — 0.005 | 1.0 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| All sites | 205 | 1.3 | <0.005 | <0.005 | 0.077 | 5.3 | 39 | 34 | 12 | 4 |
| By aquifer type: | | | | | | | | | | |
| Alluvial | 137 | .14 | <.005 | <.005 | <.005 | .8 | 4.9 | 23 | 4 | 0 |
| Bedrock | 68 | 3.6 | <.005 | .05 | 1.55 | 27 | 39 | 57 | 28 | 13 |
| By presence of $H_2S$: | | | | | | | | | | |
| Without | 164 | .55 | <.005 | <.005 | <.005 | 1.2 | 28 | 25 | 6 | 2 |
| With | 41 | 4.1 | <.005 | .2 | 2.8 | 33 | 39 | 71 | 37 | 15 |

detectable concentrations. Alluvial sites had a maximum concentration of 4.9 mg/L whereas bedrock sites had a maximum concentration of 39 mg/L; the fraction of bedrock sites with concentrations exceeding 10 mg/L was about 13 percent. Mean concentrations were 0.14 mg/L for all alluvial sites and 3.6 mg/L for all bedrock sites. Boxplots of these data are a useful way to show data distributions. Statistics shown by boxplots are illustrated in figure 8. Side-by-side boxplots comparing methane concentrations for alluvial and bedrock sites are shown in figure 9.

## Relation to Other Water-Quality Constituents

Rank correlations were made between dissolved-methane concentrations and specific conductance, pH, temperature, alkalinity, and concentrations of dissolved solids, major ions, bromide, silica, iron, and manganese, and equilibrium $CO_2$ pressure. Equilibrium $CO_2$ pressures (Drever, 1982, p. 35-58) were calculated by use of the chemical-equilibrium model described by Ball and others (1987). Correlations were done for analyses of samples from alluvial, bedrock, and combined water-quality sites. The results of these correlations indicate that no correlation coefficient (Spearman's rho, $R_s$) exceeded 0.572. The square of this value ($R_s^2 = 0.327$) indicates that less than one-third of the variation in the dissolved-methane concentrations can be related to the variation in the other constituents and properties listed. These results indicate weak or nonexistent relations between dissolved-methane concentrations and other constituents and properties. The lack of clear relations can probably be attributed to the complex variety of water-quality compositions in alluvial and bedrock aquifers.

The lack of correlation between dissolved-methane concentrations and specific conductance and dissolved-solids concentrations indicate that highly mineralized water generally is not associated with large methane concentrations. Dissolution of shales in the Animas and Nacimiento Formations contributes to large dissolved-solids concentrations. Generally, dissolved-solids concentrations in near-surface bedrock strata increase southward in the Animas River valley. Of the 24 sites having specific-conductance values exceeding 2,000 µS/cm, 10 are bedrock sites, 9 of which are located in a 7-mi reach from 2 mi north of the State line to south of Cedar Hill. Seven of these ten sites had measured methane concentrations less than 0.5 mg/L. Chemical analyses of samples from six of these ten sites indicate that sodium is the major cation and chloride and sulfate are the major anions.

The fourteen alluvial sites that had measured specific-conductance values exceeding 2,000 µS/cm are located between Cedar Hill and Aztec. Nine of these sites had no measurable methane concentrations, and the maximum measured concentration was 0.32 mg/L. The five sites with major-ion data indicate a sodium calcium sulfate water type with little chloride. Ten of the fourteen sites are located along the margin of the alluvium, indicating that most saltier alluvial water probably results from bedrock discharge, inflow from tributary valleys, and dissolution of bedrock minerals. The remaining four sites probably are located immediately down gradient from bedrock-discharge points where lower shale contacts are exposed to the alluvium.

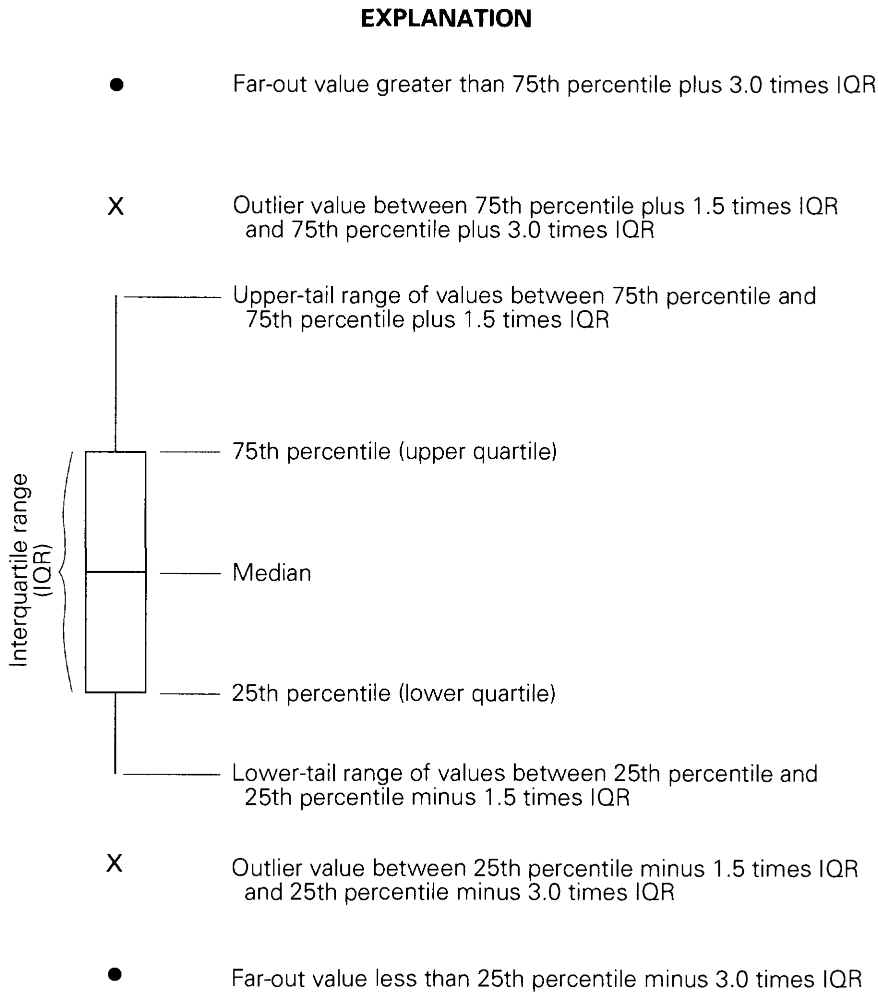



**Figure 8.** Statistics shown by a boxplot.

Water-quality measurements indicate a relatively strong association between dissolved methane and hydrogen sulfide ($H_2S$). Only 41 of 164 (25 percent) sites without $H_2S$ had measurable methane concentrations (the mean concentration was about 0.55 mg/L), whereas 29 of 41 (about 71 percent) sites with $H_2S$ had measurable methane concentrations (the mean concentration was about 4.1 mg/L). Because produced gas in the study area is virtually free of $H_2S$ (Mark Weems, COGCC, and Frank Chavez, NMOCD, oral commun., 1991), the association between dissolved methane and $H_2S$ may be attributed to a combination of several processes:

1. Methane that has migrated vertically from deep reservoirs can be oxidized by dissolved sulfate, producing $H_2S$ and $CO_2$. Kelly and others (1985) demonstrated that methane-affected water wells in the vicinity of a leaking gas well had smaller sulfate concentrations and greater concentrations of sulfide and alkalinity compared to unaffected water wells. These investigators confirmed this oxidation process by laboratory experiments and a thermodynamic-equilibria simulation.

2. $H_2S$ may be cogenerated with biogenic gas. Oremland and Taylor (1978) demonstrated simultaneous methane generation and sulfate reduction. Overlapping distributions of methanogenic and sulfate-reducing bacteria in reducing sediments and coexistence of these bacteria in mixed continuous cultures were reported by Cappenberg (1975). All three predominantly biogenic-gas samples collected from water wells for this study (discussed in the section "Analysis of Specific Gas Samples") contained abundant $H_2S$.

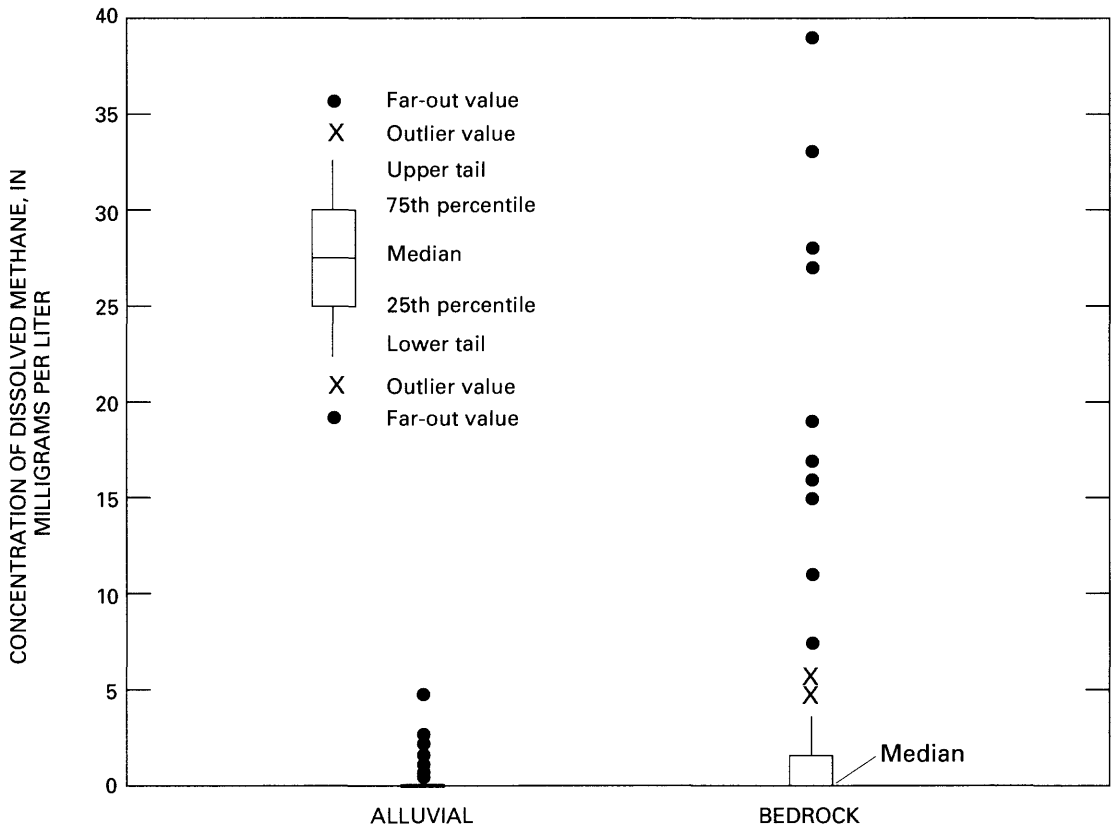



**Figure 9.** Dissolved-methane concentrations for alluvial and bedrock ground-water sites.

3. Migrating natural gas may scavenge $H_2S$ from sulfate-reducing zones in deeper strata or lateral to water-well sites or may invade water-yielding sulfate-reducing zones around water-well boreholes.

Information is not available to allow an assessment of the relative predominance of these processes in the study area.

### Seasonal Variation in the Cedar Hill Area

Following initial sampling during September 1990, 20 randomly selected, valley-fill wells in the Cedar Hill area were resampled during February 20-25, 1991, to document any short-term seasonal variation in dissolved-methane concentrations. The hypothesis tested was whether water-level declines during winter allow more gas to migrate from bedrock, causing greater dissolved-methane concentrations. Water levels declined 1.6 to 29.4 ft in the 16 measured wells between September 1990 and February 1991 because of cutoff of diverted ditch water in early fall and pumping from numerous household wells. Methane concentrations were less than 0.005 mg/L during both sampling periods at 12 of the 20 sites, which indicates no measurable increase in methane concentrations. Concentrations increased 0.036 to 0.87 mg/L (mean increase 0.30 mg/L) at five sites but decreased about 0.004 to 0.71 mg/L (mean decrease 0.45 mg/L) at three sites. On the basis of these data, no significant change in methane concentrations during the 6 months can be concluded.

## METHANE IN SOIL GAS

At 192 of the 205 ground-water sites, soil-gas-methane concentrations were measured in the vicinity of each water well or spring (generally 50 to 100 ft down valley). Soil-gas-methane concentrations were measured at four soil seeps and adjacent to 352 gas wells (usually within 1 ft of each casing at several locations). These data are presented in Chafin and others (1993). This section: 1) compares soil-gas-methane concentrations at ground-water sites to methane concentrations in the water at those sites, 2) describes soil-gas-methane concentrations at soil seeps and at gas wells, 3) describes the relation of soil-gas-methane concentrations at gas wells to the age of those wells, and 4) compares soil-gas-methane concentrations at ground-water sites to those at gas wells.

## Ground-Water Sites

Soil-gas-methane concentrations at ground-water sites seldom were greater than the reporting limit of 0.005 mg/$L_g$ (gas-volume basis), even at sites where large dissolved-methane concentrations in the ground water were measured. Soil-gas-methane concentrations equaled or exceeded the reporting limit at five sites (3 percent), with a maximum concentration of 0.5 mg/$L_g$. This distribution indicates that background soil-gas-methane concentrations were less than 0.005 mg/$L_g$. The lack of a direct relation between dissolved-methane concentrations in ground water and methane concentrations in soil gas can be attributed to several factors: (1) dissolved gas at bedrock sites typically comes from confined strata that do not permit gas to enter the soil column; (2) concentrations of gas in alluvium generally are too small to permit substantial flux of gas into the soil column; and (3) most methane entering the soil column is consumed by methanotrophic microorganisms (Adamse and others, 1972; Mancinelli and others, 1981). Striegl and Ishii (1989) determined that bacterial consumption of methane was important in soils overlying radioactive wastes in north-central Illinois. The lack of a relation between ground-water-methane concentrations and nearby soil-gas-methane concentrations indicates that soil-gas surveys generally are not useful to delineate areas in the study area where ground water is charged with gas.

## Soil Seeps

Soil-gas-methane measurements were used to document four gas seeps in open fields in the study area at 31N-10W-05AAA (400 mg/$L_g$ methane), 32N-10W-34BCB (360 mg/$L_g$), 32N-09W-06BCA (570 mg/$L_g$), and 32N-10W-01ADB (330 mg/$L_g$). Two of these seep sites were reported by landowners and two were discovered by lack of vegetation and confirmed by soil-gas measurements. These seeps were manifested as bare spots in the grass that were 5 to 10 ft across. The three seep sites at 31N-10W-05AAA, 32N-10W-34BCB, and 32N-09W-06BCA are located in the lower valley near the river. At two of these three sites, several seeps were observed over elongated areas about 250 ft and 600 ft long, respectively, and were aligned nearly parallel to the river. The locations and orientations of these seeps indicate that they emanate from abandoned river channels that cut through confining shale and are now filled with coarse alluvium. The fourth seep was located on a terrace at Bondad. A concentration of 330 mg/$L_g$ was measured at this seep on October 24, 1990, but measurements in April 1991 indicated less than 0.005 mg/$L_g$.

## Gas Wells

Statistics describing soil-gas-methane concentrations measured adjacent to gas-well casings are summarized in table 2. The reporting limit of 0.005 mg/$L_g$ was equaled or exceeded by 40 percent of the measurements, and the mean concentration was 29 mg/$L_g$. Concentrations of at least 100 mg/$L_g$ were measured at 25 wells (7 percent) up to a maximum value of 1,200 mg/$L_g$, which was measured adjacent to a gas well at 33N-09W-31CCD. This well was left uncased (except for surface casing) and unplugged since it was drilled to a depth of 2,240 ft in 1937. Gas flow along the outside of the surface casing was forceful enough to overpressure sampling equipment and cause a measured soil-gas-methane concentration about twice that of pure methane at ambient temperature and pressure (about 600 mg/$L_g$).

### Relation to Age of Gas Wells

To determine whether soil-gas-methane concentrations have some relation to the age of gas wells, soil-gas measurements were divided into two groups on the basis of the completion year of the wells. Those gas wells completed during 1937-76 were compared to those completed during 1977-90 to divide the data into two nearly equal parts. Summary statistics for these two groups are listed in table 2, and side-by-side boxplots are shown in figure 10.

Gas wells completed during 1937-76 have a greater mean soil-gas-methane concentration (32 mg/$L_g$) than do gas wells completed during 1977-90 (25 mg/$L_g$). However, by not including the 1,200-mg/$L_g$ concentration for the gas well at 33N-09W-31CCD from the 1937-76 group, the mean would be 26 mg/$L_g$. The 1977-90 group had a greater 75th-percentile value of 0.3 mg/$L_g$ compared to 0.03 mg/$L_g$ and had slightly greater percentages of concentrations equaling or exceeding 0.005 and 10 mg/$L_g$

**Table 2.** Summary statistics for soil-gas-methane concentrations measured at ground-water sites and adjacent to gas-well casings

[N, number of sites; $Q_{.25}$ (for example), quantile with subscripted number showing fraction of samples with concentration less than or equal to concentration shown; <, less than]

| Site category | N | Concentration of soil-gas methane (milligrams per liter of gas) | | | | | | Percent of samples equaling or exceeding concentration, in milligrams per liter of gas | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Mean | Quantiles | | | | Maximum | | | |
| | | | $Q_{.25}$ | $Q_{.50}$ | $Q_{.75}$ | $Q_{.95}$ | | 0.005 | 10 | 100 |
| Ground water | 192 | <0.005 | <0.005 | <0.005 | 0.09 | <0.005 | 0.5 | 3 | 0 | 0 |
| All gas wells | | 29 | <.005 | <.005 | .009 | 200 | 1,200 | 40 | 14 | 7 |
| Gas wells by year completed: | | | | | | | | | | |
| 1937-76 | 187 | 32 | <.005 | <.005 | .03 | 240 | 1,200 | 34 | 13 | 7 |
| 1977-90 | 165 | 25 | <.005 | <.005 | .3 | 180 | 610 | 47 | 14 | 7 |

compared to the 1937-76 group. However, overall concentrations are not significantly different between groups.

### Comparison to Concentrations at Ground-Water Sites

A comparison of soil-gas-methane concentrations measured adjacent to gas-well casings and at ground-water sites was made to determine possible migration pathways of near-surface gas. Summary statistics for these two data groups are listed in table 2, and side-by-side boxplots are shown in figure 11.

Concentrations of soil-gas methane determined adjacent to gas-well sites equaled or exceeded 0.005 $mg/L_g$ in 40 percent of measurements, whereas concentrations determined at ground-water sites equaled or exceeded 0.005 $mg/L_g$ in only about 3 percent of measurements. Maximum concentrations were 1,200 $mg/L_g$ for gas-well sites and 0.5 $mg/L_g$ for ground-water sites. Concentrations at gas-well sites equaled or exceeded 100 $mg/L_g$ at 7 percent of the sites.

## GEOCHEMISTRY OF GASES

Methane delta-carbon-13 ($\partial^{13}C_1$) values and molecular compositions are important tools that are used to characterize the geochemistry of hydrocarbon gases.

$\partial^{13}C_1$ values, in permil (‰), are defined by (Faure, 1977, p. 379):

$$\partial^{13}C_1 = \left[\frac{(^{13}C_1/^{12}C_1)_{spl} - (^{13}C/^{12}C)_{std}}{(^{13}C/^{12}C)_{std}}\right] \times 10^3‰, \quad (1)$$

where

$(^{13}C_1/^{12}C_1)_{spl}$

= carbon-13 to carbon-12 mole ratio of methane sample, and

$(^{13}C/^{12}C)_{std}$

= carbon-13 to carbon-12 mole ratio of reference standard.

The reference standard is $CO_2$ gas generated by reacting belemnites of the Peedee Formation of South Carolina with phosphoric acid.

Hydrocarbon-gas molecular composition is expressed by the wetness fraction (W), defined by Rice and others (1989, p. 606-607) as:

$$W = C_1/C_{1\text{-}5}, \quad (2)$$

where

$C_1$ = mole percentage of methane, and

$C_{1\text{-}5}$ = sum of mole percentages of methane, ethane, propane, butane, and pentane.

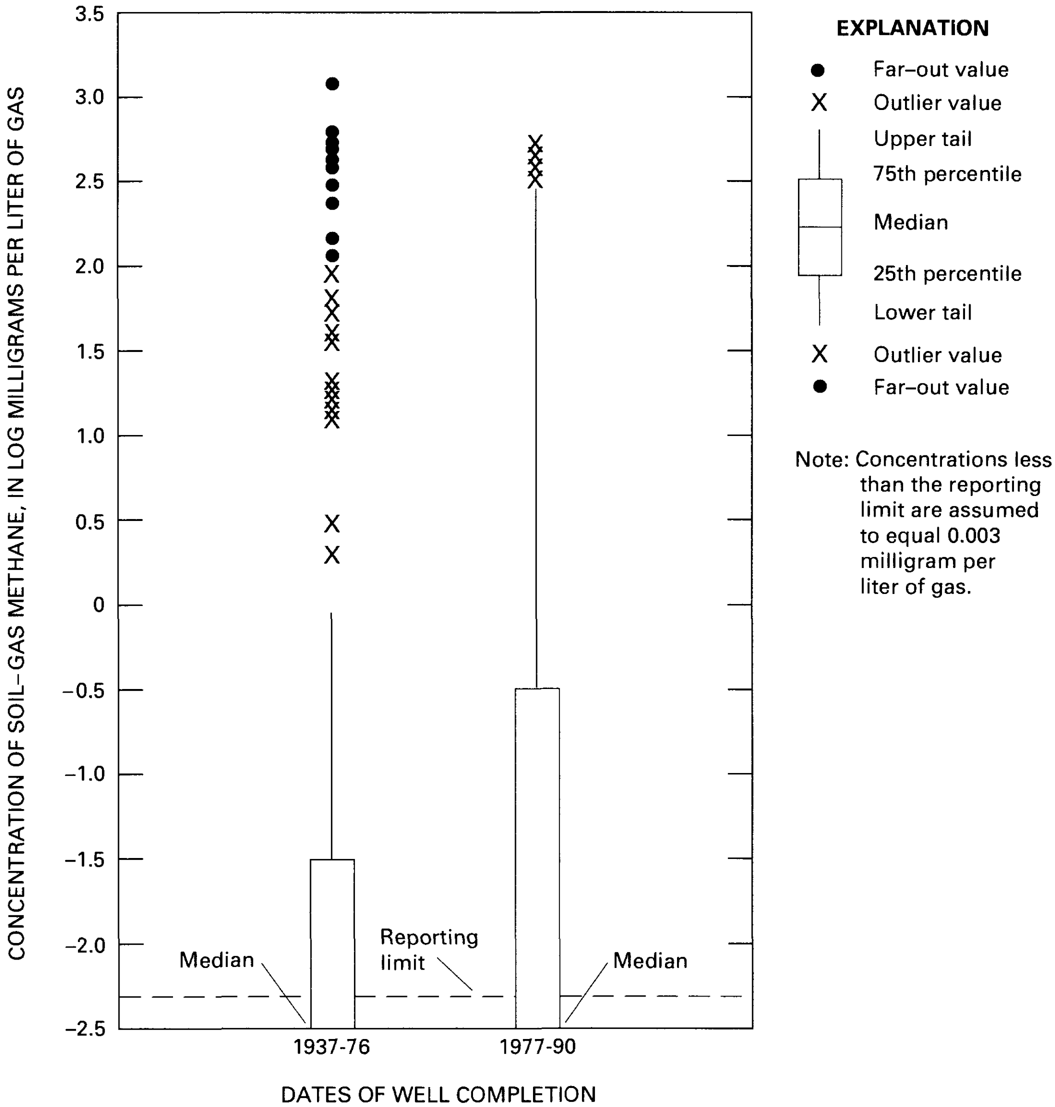



**Figure 10.** Soil-gas-methane concentrations measured adjacent to gas-well casings completed during 1937-76 and 1977-90.

Gases with wetness values near 1.00 are considered to be dry. Gases with smaller wetness values (usually <0.95) are considered to be wet.

Natural gas from the San Juan Basin consists of two end-member types: biogenic (also called bacterial or microbial) and thermogenic (Rice and others, 1989). These two types of gas have distinctively different signatures of $\partial^{13}C_1$ values and gas-wetness fractions, (fig. 12, table 3). Following a background discussion of these two types of gas, this section will discuss secondary processes that can affect the geochemistry of natural gas subsequent to migration from reservoirs.

### Biogenic Gas

Biogenic gas is produced during bacterial decomposition of organic matter in an environment that has relatively shallow burial depths, is free from oxygen, and is deficient in sulfate (Rice and Claypool, 1981). Biogenic gas contains small fractions of hydrocarbons heavier than methane ($C_{2+}$ hydrocarbons), generally has wetness fractions greater than 0.98, is relatively enriched in carbon-12, and has $\partial^{13}C_1$ values generally less than -55 ‰ (Rice and Claypool, 1981) (fig. 12).

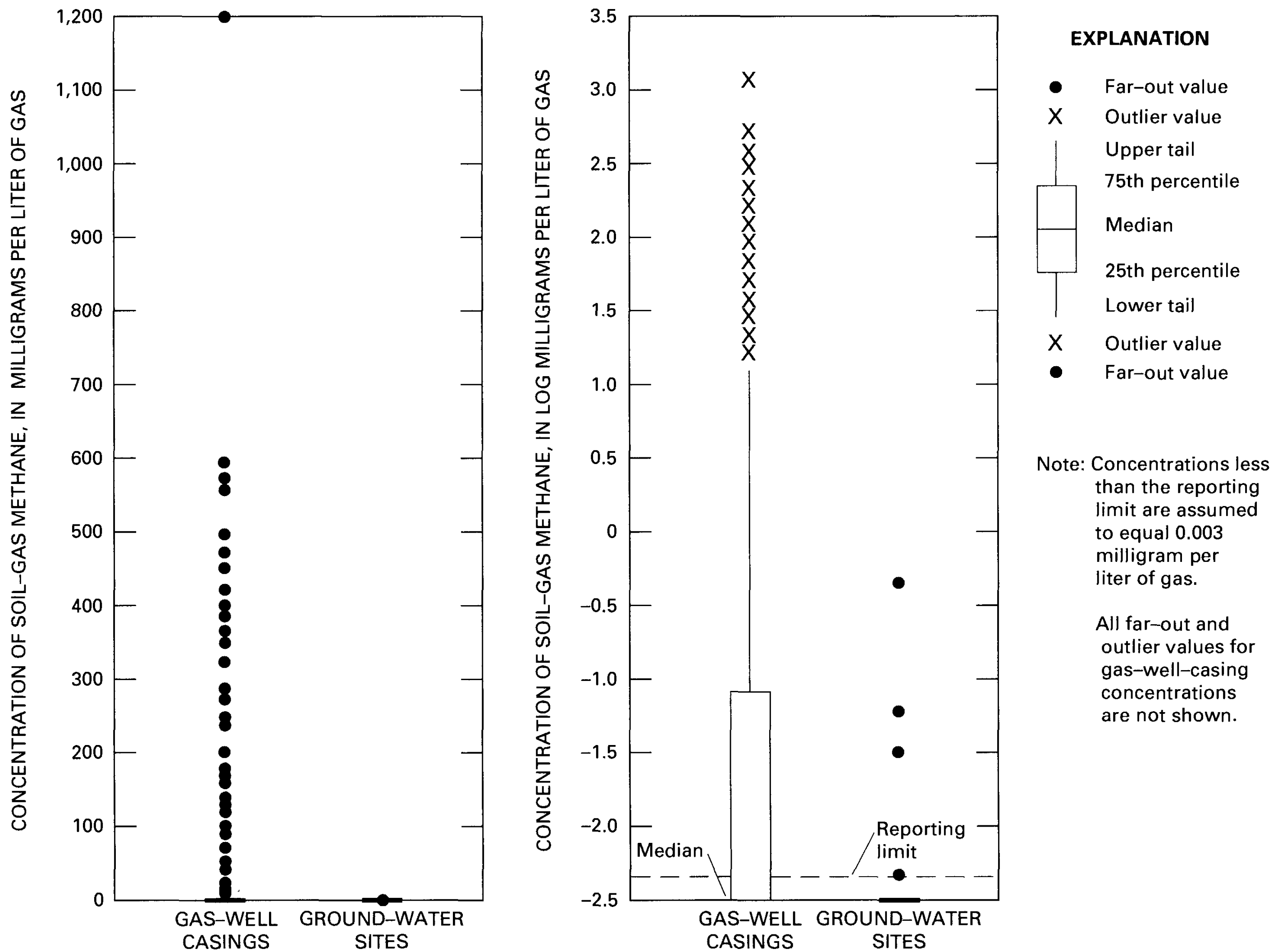



**Figure 11.** Soil-gas-methane concentrations measured adjacent to gas-well casings and at ground-water sites.

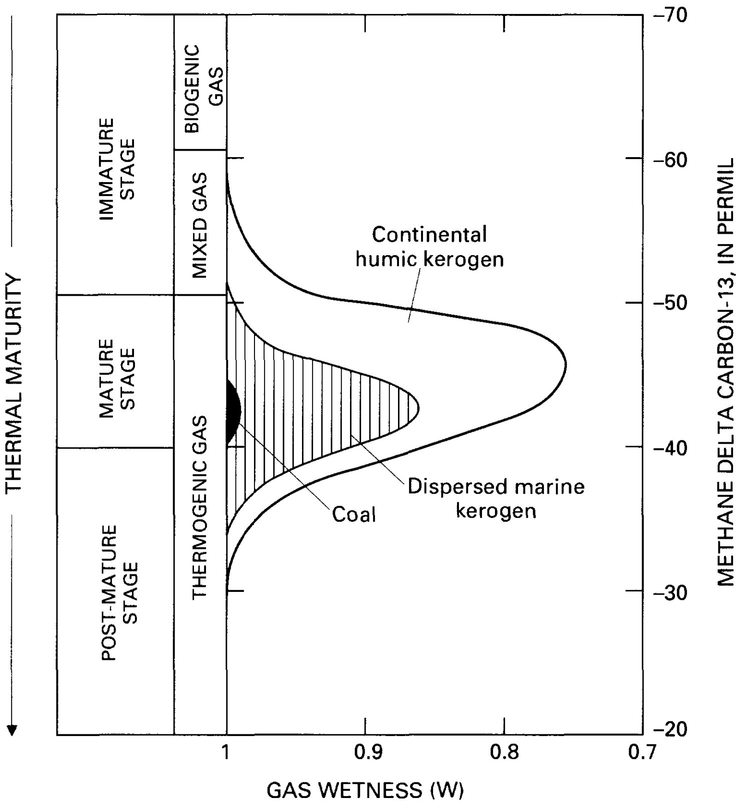



**Figure 12.** Molecular and methane-carbon-isotope compositions of natural gases from different environments and organic-matter types in the San Juan Basin (modified from Rice and others, 1989, p. 611).

Some investigators report biogenic methanes with $\partial^{13}C_1$ values as large as -40‰, which would potentially overlap values for thermogenic methane that is produced beneath the study area and would complicate identification of gas sources. A review of biogenic methanogenic processes indicates that $\partial^{13}C_1$ values in the -40 to -50‰ range are not likely for biogenic gas in bedrock beneath the study area and that $\partial^{13}C_1$ values can be used to distinguish between biogenic and produced thermogenic gases. Whiticar and others (1986) used carbon and hydrogen isotopes to characterize the two pathways of methane formation: acetate fermentation and $CO_2$ reduction. These investigators concluded that $CO_2$ reduction usually generates methane in the sulfate-free zone of relatively shallow marine sediments, producing methane having $\partial^{13}C_1$ values in the -110 to -60‰ range and delta-deuterium ($\partial D_1$) values in the -250 to -170‰ range. Methane from relatively recent freshwater environments was considered to generally result from acetate fermentation and have $\partial^{13}C_1$ values in the -65 to -50‰ range and $\partial D_1$ values in the -400 to -250‰ range. Schoell (1988) reviewed $\partial^{13}C_1$ and $\partial D_1$ values reported for various aqueous environments and summarized similar $\partial^{13}C_1$ and $\partial D_1$ ranges for methanogenic pathways as did Whiticar and others (1986), except that Schoell (1988, p. 3) extended the acetate-fermentation $\partial^{13}C_1$ range to values as heavy as about -41‰ and the $CO_2$-reduction $\partial D_1$ range to -150‰. Schoell (1988, p. 3) concluded that all known environments producing fermentation methane are young sediments with input of fresh organic debris. He further concluded (p. 4) that fermentation gases are very unlikely to become trapped in deeper strata because these gases are predominantly lost to the atmosphere soon after generation. Because the organic matter in the Animas and Nacimiento Formations is more than 50 million years old, it is unlikely that fermentation

**Table 3.** Isotopic and molecular composition of natural gas

[Gas wetness, W, is defined as percentage of methane ($C_1$) divided by the sum of percentages of methane, ethane, propane, butane, and pentane ($C_{1\text{-}5}$): $W=C_1/C_{1\text{-}5}$; $\partial^{13}C_1$, delta carbon-13 of methane; ‰, permil; $\partial D_1$, delta deuterium of methane; <, less than; >, greater than; ~, approximately]

| Gas type | $\partial^{13}C_1$ (‰) | Gas wetness, W | Other characteristics |
|---|---|---|---|
| Biogenic: | | | |
| Acetate fermentation[1] | [2]-65 to [3]-41 | [4]0.98 to 1.0 | $\partial D_1$ = [3]-400 to -250 |
| $CO_2$ reduction | [2]-110 to -60 | [4]0.98 to 1.0 | $\partial D_1$ = [3]-250 to -150 |
| Thermogenic: | | | |
| Earliest mature | [5]-60 to -50 | [5]~0.9 to 1.0 | [5]Associated with earliest oil production |
| Early mature | [5]-53 to -43 | <0.95 | [5]Associated with peak oil production |
| Late mature | [5]-43 to -35 | <0.95 | [5]Associated with condensate |
| Post mature | [5]>-40 | ~0.98 to 1.0 | [5]Nonassociated dry gas |

[1]No data from the study area match these ranges for both $\partial^{13}C_1$ and $\partial D_1$.
[2]Whiticar and others, 1986
[3]Schoell, 1988
[4]Rice and Claypool, 1981
[5]Schoell, 1983

methane is being produced in these formations and that biogenic methane with $\partial^{13}C_1$ values greater than -50‰ can be found in them. Furthermore, $\partial D_1$ values of -162, -150, and -208‰ (Chafin and others,1993) were measured for the only three predominantly biogenic gases collected for this study—indicating that these methanes largely originated by $CO_2$ reduction.

## Thermogenic Gas

Thermogenic gas is produced from solid and liquid organic matter by thermal degradation at high temperatures and long heating periods associated with deep burial of sediments (Rice and others, 1989). The progression of hydrocarbons generated with increasing time and temperatures, as described by Rice and Claypool (1981), is illustrated in figure 13. At depths generally greater than about 1 km (3,281 ft), biogenic-methane production gradually gives way to production of thermogenic methane, which is not produced in substantial quantities until temperatures of about 100°C are attained. In the early mature stage (fig. 13), gas contains substantial quantities of $C_{2+}$ hydrocarbons and is associated with oil. Substantial quantities of oil usually require sapropelic (generally marine) source rocks (Rice, 1983, p. 1208). Schoell (1983, p. 2231) concludes that the first methane associated with petroleum has $\partial^{13}C_1$ values in about the -60 to -50‰ range, and methane formed during peak oil generation has values of about -53 to -43‰, with oil generation ending at about -40‰ (Schoell, 1983, fig. 1). During the late-mature thermogenic stage, petroleum begins to be degraded and the primary products are wet gas and condensate (non-oil hydrocarbons that are gas under pressure at depth but become liquid at the surface). Schoell (1983, fig. 1) shows this stage to occur over a $\partial^{13}C_1$ range of about -43 to -35‰. At the post-mature thermogenic stage, dry gas is produced by the degradation of hydrocarbons heavier than methane. Schoell (1983, fig. 1) considers this stage to occur at $\partial^{13}C_1$ values greater than about -40‰.

Coal rank is another useful indication of thermal maturity of hydrocarbons. Coal vitrinite reflectance ($R_o$) values are a commonly used indicator of coal rank. $R_o$ values of 0.6 (Galimov, 1988, p. 91) to 0.65 percent (Waples, 1980, p. 921) are associated with the beginning of the oil-associated thermogenic-gas stage.

Terrestrial organic matter of humic composition produces thermogenic hydrocarbon products that do not conform to the trend described for sapropelic organic matter. Galimov (1988, p. 91) describes methane with $\partial^{13}C_1$ values of -50 to -46‰ that formed from predominantly humic organic matter at thermal maturities ($R_o$ values approximately 0.4 to 0.55 percent) less

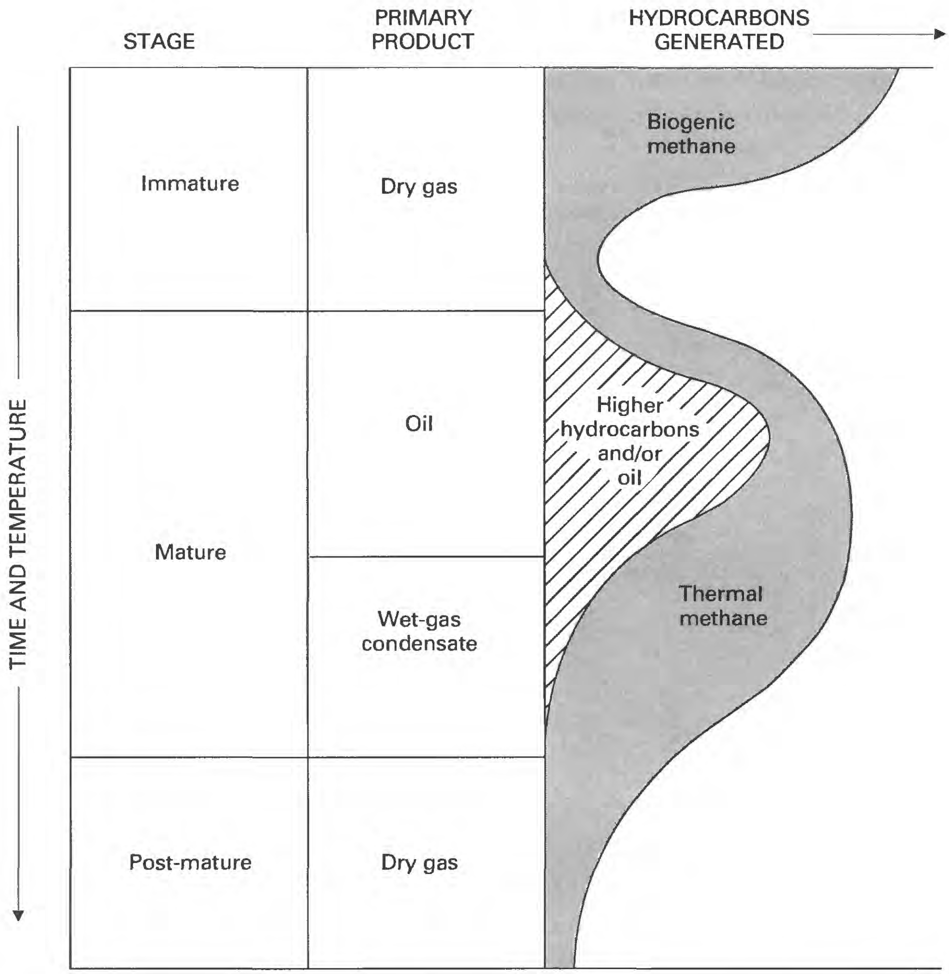



**Figure 13.** Generation of hydrocarbons with increasing time and temperature (from Rice, 1983, p. 1205).

than that at which early thermogenic gas forms from sapropelic organic matter. Galimov (1988, p. 91) further concluded that humic organic matter produces condensate at thermal maturities less than that at which sapropelic organic matter produces substantial quantities of oil.

Rice (1983) related natural-gas compositions in the San Juan Basin to thermal maturities. He reported (p. 1202-1203) that oil production largely is limited to the Mancos Shale, Dakota Sandstone, and Mesaverde Group on shelf areas adjacent to the central basin and along the southern part of the central basin, where formation burial depths are less than in the structurally lower northern central basin. Rice (1983, p. 1216) concluded that, in general, gases in the San Juan Basin become isotopically heavier and drier with increasing depth, except that, in general, gases derived from marine organic matter are wetter and isotopically lighter than gases derived from terrestrial organic matter.

Rice and others (1989) described coal-bed gas from the Fruitland Formation, generally the uppermost producing stratum in the northern San Juan Basin. On the basis of coal vitrinite reflectance ($R_0$) values exceeding 0.7 percent, they concluded that Fruitland coal-bed gas in the northern central basin is thermogenic in origin. This gas shows little variation in $\partial^{13}C_1$ values (-40.5 to -43.6‰), W values generally greater than 0.99, and generally contains substantial quantities of $CO_2$ (as much as 6 percent). A map of $R_0$ values (Rice and others, 1989, p. 605, fig. 5) indicates that these values increase steeply in a northeast direction and that the 0.7-percent line lies about halfway between Cedar Hill and Aztec, New Mexico. Gas samples south of this line (Rice and others, 1989, p. 608-9) show rapidly decreasing wetness values (0.871-0.929). Rice (1983, p. 1216) concluded that greater coal maturities in the northern part of the basin resulted from an increased geothermal gradient associated with emplacement of batholiths in the San Juan Mountains during Oligocene times, when maximum hydrocarbon generation occurred.

Lenticular channel sandstones above the basal coals in the Fruitland Formation locally produce small amounts of relatively wet gas not associated with oil (Rice and others, 1989). One sample from about 10 mi west-southwest of Bondad had a $\partial^{13}C_1$ value of 39.5‰ (W = 0.941).

## Secondary Processes Affecting Gas Composition

Subsequent to migration from gas reservoirs, several secondary processes can alter molecular and isotopic compositions of natural gas and complicate identification of gas sources. Schoell (1983) lists mixing, migration, and oxidation as processes that change molecular and isotopic compositions of hydrocarbon gases. Mixing of gases results in linear and proportional changes in isotopic composition (Schoell, 1983) and in chemical composition.

Generally, migration does not cause substantial changes in $\partial^{13}C_1$ values (Bernard and others, 1977; Coleman and others, 1977; Stahl and others, 1977). This fact facilitates the use of $\partial^{13}C_1$ values to determine sources of gas. In many cases, however, substantial changes in gas composition caused by migration limit the use of gas-wetness values to determine sources of gas. A common type of change is enrichment of methane in gas that migrates through sediments (Schoell, 1983) because of the smaller volatilities of $C_{2+}$ hydrocarbons. This process is aided by solubilization of ethane, usually the most abundant component heavier than methane. Ethane is about one-third more soluble than methane on a volume-to-volume basis (Mackay and Shiu, 1981, p. 1182). More rapid volatilization of methane from a gas-charged stratum leaves the residual gas body enriched in $C_{2+}$ hydrocarbons (aging distillation), which causes smaller wetness values.

Oxidation of natural gas in near-surface environments increases $\partial^{13}C_1$ values and can complicate the use of $\partial^{13}C_1$ values to determine gas sources. The effects of bacterial oxidation on wetness values for near-surface gas are uncertain and difficult to separate from migration effects, although James and Burns (1984) interpreted the compositions of some examples of deep, reservoired gas to indicate preferential oxidation of $C_{2+}$ components, resulting in greater wetness values.

Oxidation occurs in aerobic (containing oxygen) and anaerobic (lacking oxygen) environments. Coleman and others (1981) reported that $\partial^{13}C_1$ values were increased by as much as 23‰ in aerobic laboratory experiments at 11.5°C; $\partial^{13}C_1$ values were increased about 15‰ with 30 percent of original methane remaining and about 7‰ with 50 percent remaining. Barker and Fritz (1981b) experimentally determined that aerobic oxidation at about 23°C increased $\partial^{13}C_1$ values as much as 22‰, but only 5 to 7‰ with one-third of original methane remaining. These authors cautioned against applying these maximum shifts to natural systems because the temperatures and nutrient concentrations used in the experiments were higher than those expected in most ground waters. Furthermore, both of these experiments featured oxygen replenishment and were closed to input of additional methane, conditions not often duplicated in the shallow ground-water environment, where oxidation of migrating gas depletes oxygen. Continuous addition of methane would dilute $\partial^{13}C_1$ increases caused by oxidation, and oxygen depletion would terminate aerobic oxidation. Barker and Fritz (1981a, p. 1807-9) report near-surface ground-water samples in Canada that contained oxidized methane, considered to be thermogenic in origin, and that appeared to have maximum $\partial^{13}C_1$ shifts between +10.9‰ and +18.5‰, depending on the presumed $\partial^{13}C_1$ value of the original methane. A sample from one water well exhibited a +7.2‰ shift in $\partial^{13}C_1$ when the methane concentration was decreased about fourfold.

Anaerobic oxidation occurs by bacterial reduction of sulfate, producing hydrogen sulfide ($H_2S$). Alperin and Reeburgh (1988) measured anaerobic oxidation shifts in $\partial^{13}C_1$ values of about +5‰ to +8‰ in marine sediments. Whiticar and Faber (1986, p. 763) reported that fractionation of $\partial^{13}C_1$ values for marine and brackish sediments was less than 4‰ until residual methane concentrations decreased to less than 10 percent.

An overview of these secondary processes indicates that gas-wetness and $\partial^{13}C_1$ values are not always reliable indicators of gas sources. This conclusion is especially true for gas-wetness values, which can be increased (by mixing, migration, and oxidation) or decreased (by mixing and aging distillation). $\partial^{13}C_1$ values can be increased (by mixing and oxidation) or decreased (by mixing). These effects on gas-wetness and $\partial^{13}C_1$ values underscore the importance of incorporating ancillary information (especially gas-well construction or remediation records) in a study of gas sources and migration pathways.

## ANALYSIS OF ISOTOPIC AND MOLECULAR COMPOSITION OF GASES FROM WATER, SOIL, GAS-WELL CASINGS, AND CATHODIC-PROTECTION WELLS

This section examines potential sources of gases in ground water and soil by comparing methane-carbon-isotope and molecular compositions to those for nearby produced gases and the known range of values for biogenic gases and by incorporating pertinent information about gas-well construction or leaks. This examination is preceded by an assessment of the types of indigenous gas possibly existing in the Animas and Nacimiento Formations prior to gas-well development.

Gas was collected for analyses of isotopic and molecular composition from 16 water samples, from 3 open-field soil seeps (previously discussed), from the soil adjacent to 11 gas wells that had indicated elevated soil-gas-methane concentrations, and from 30 gas wells. The data for these samples are reported in Chafin and others (1993). Additional analyses of gas samples collected by COGCC and NMOCD in 1989 and 1990 from surface casings, *intermediate casings*, and *production casings* of gas wells, and from cathodic-protection wells, also are used in the assessment made in this study. These additional samples provide more information about sources of gases potentially affecting ground-water quality in the study area. All gas samples were analyzed by the U.S. Geological Survey. Gas-wetness fractions and $\partial^{13}C_1$ values for these samples are summarized in table 4, and sampling locations are shown on plate 3.

Produced-gas samples collected from gas wells and compiled for this study (table 4) generally exhibit the trends described for the San Juan Basin by Rice (1983). These samples (excluding gas from Fruitland coals) have $\partial^{13}C_1$ values ranging from -42.98 to -31.86‰ and W values ranging from 0.843 to 1.00. Values of $\partial^{13}C_1$ for each producing formation decrease southward, indicating decreasing gas maturity. Locally, $\partial^{13}C_1$ values for production gas generally increase with depth in the following order of producing unit: coals in the Fruitland Formation, Pictured Cliffs Sandstone, Mesaverde Group, and Dakota Sandstone. Differences in $\partial^{13}C_1$ values between formations are more pronounced in the Colorado part of the study area than in the New Mexico part, reflecting a steeper maturity profile. All gas samples from the Dakota Sandstone exhibit dry W values (>0.99), indicating post-mature gas. Gas samples from the Mesaverde Group indicate a post-mature stage in Colorado and a mature, wet gas-condensate stage in New Mexico. Gas samples from the Pictured Cliffs Sandstone indicate a mature stage, which Rice and others (1989, p. 611) state should be oil-associated, except for the absence of sapropelic kerogen in the source rocks. Coal-bed-gas samples from the Fruitland Formation throughout the study area all have $\partial^{13}C_1$ values in the -43.56 to -41.91‰ range and W values exceeding 0.99 (except for the southernmost sample), indicating a mature-gas stage. The southernmost sample from the Fruitland Formation has a W value of 0.904, probably indicating a substantial fraction of early-thermogenic gas.

### Indigenous Gas in the Animas and Nacimiento Formations

To identify probable sources of gases in ground water and soil, it is necessary to determine if the near-surface Animas and Nacimiento Formations contain indigenous methane with $\partial^{13}C_1$ values that overlap those from deeper gas-producing formations. The following assessment considers gas occurrences in the Nacimiento Formation, revised estimates of the burial depths of the near-surface Animas and Nacimiento Formations during the main gas-generation stage, and concepts of gas maturity.

COGCC records list one gas well producing from the Nacimiento Formation in the San Juan Basin. This well is located at 32N-08W-03 (about 9 mi east of Bondad) and has listed producing intervals in the Dakota Sandstone, Mesaverde Group, and Nacimiento Formations. The depth of the upper producing interval (2,306 to 2,314 ft) and the driller's log indicate that this interval probably is in the upper Kirtland Shale, not the Nacimiento Formation. A gas analysis from this interval shows wet gas (W = 0.932) with a $\partial^{13}C_1$ value of -39.3‰ (Dudley Rice, U.S. Geolological Survey, written commun., 1993). Rice concluded that the gas probably is too mature to have been generated in the Nacimiento Formation and that it probably migrated from deeper rocks. Construction details indicate possi-

**Table 4.** Gas-wetness fractions and methane-carbon-isotope ratios for selected gas samples from ground water, soil and river seeps, soil adjacent to gas-well casings, and from surface, intermediate, and, production casings of gas wells

[Gas wetness, W, is defined as percentage of methane ($C_1$) divided by the sum of percentages of methane, ethane, propane, butane, and pentane ($C_{1-5}$): $W = C_1/C_{1-5}$; $\partial^{13}C_1$, delta carbon-13 of methane; ‰, permil; $\partial^{13}C_1$ values are reported relative to the Peedee belemnite marine carbonate standard; PC, gas-well production casing; SC, gas-well surface casing; IC, gas-well intermediate casing; CPW, cathodic-protection well]

| Site number (see plate 3) | Water well or land owner, gas-well formation, or site description | Gas source | Land-net location | Gas wetness, W | $\partial^{13}C_1$ (‰) | Data source |
|---|---|---|---|---|---|---|
| | | | **NORTHERN ZONE** | | | |
| 1 | Fruitland Coal Gas Well | PC | 34N-09W-08BDB | 1.00 | -43.20 | (1) |
| 2 | Charles Weekly | Water | 34N-09W-07ADC | 1.00 | -59.66 | (1) |
| 3 | Mesaverde Gas Well | PC | 34N-10W-36BDB | .984 | -35.24 | (1) |
| 4 | Fruitland Coal Gas Well | PC | 34N-10W-36ADB | .998 | -43.56 | (1) |
| 5 | Ron Ollier | Water | 34N-10W-36CAB | 1.00 | -37.16 | (1) |
| 6 | Dakota Gas Well | PC | 34N-10W-36DBD | .998 | -31.86 | (1) |
| | | | **SUNNYSIDE MESA ZONE** | | | |
| 7 | Mesaverde Gas Well | Casing soil | 33N-10W-01CDA | .986 | -41.81 | (1) |
| | Mesaverde Gas Well | PC | 33N-10W-01CDA | .957 | -36.85 | (1) |
| 8 | Fruitland Coal Gas Well | PC | 33N-10W-13BBD | .997 | -42.37 | (1) |
| 9 | Terry Obery | Water | 33N-10W-13DDC | 1.00 | -30.73 | (1) |
| 10 | Dakota Gas Well | PC | 33N-10W-24AAC | .996 | -32.89 | (1) |
| 11 | Mesaverde Gas Well | PC | 33N-10W-24AAC | .967 | -37.68 | (1) |
| | | | **NORTH BONDAD ZONE** | | | |
| 12 | Dakota Gas Well | PC | 33N-10W-24CBD | .998 | -33.04 | (1) |
| 13 | Patty Haneman | Water | 33N-10W-25BAC | .982 | -41.96 | (1) |
| 14 | Mesaverde Gas Well | Casing soil | 33N-10W-25ABD | .869 | -35.87 | (1) |
| | Mesaverde Gas Well | PC | 33N-10W-25ABD | .954 | -38.14 | (1) |
| 15 | John Gamble | Water | 33N-10W-25ADB | .975 | -36.96 | (1) |
| 16 | Fruitland Coal Gas Well | PC | 33N-10W-25DDB | .995 | -41.91 | (1) |
| | | | **SOUTH BONDAD ZONE** | | | |
| 17 | Jack Kloepfer | Water | 33N-10W-36ACD | .870 | -41.49 | (1) |
| 18 | Dakota Gas Well | Casing soil | 33N-10W-36DAC | .888 | -42.73 | (1) |
| | Dakota Gas Well | PC | 33N-10W-36DAC | 1.00 | -32.99 | (1) |
| 19 | Carl Weston | Water | 32N-09W-31CCC | .983 | -41.73 | (1) |
| 20 | Fruitland Coal Gas Well | PC | 33N-09W-31CCD | .995 | -42.76 | (2) |
| 21 | Mesaverde Gas Well | PC | 32N-09W-06BBD | .974 | -34.56 | (2) |
| | Mesaverde Gas Well | SC | 32N-09W-06BBD | .992 | -41.61 | (2) |
| 22 | Lewis Gas Well | PC | 32N-09W-06BBD | .946 | -37.58 | (2) |
| | Lewis Gas Well | SC | 32N-09W-06BBD | .994 | -38.52 | (2) |
| 23 | Maurice Walter | Water | 32N-10W-01AAD | 1.00 | -25.20 | (1) |
| 24 | Fruitland Coal Gas Well | PC | 32N-10W-01AAC | .998 | -42.22 | (1) |
| 25 | Mesaverde Gas Well | PC | 32N-10W-01ADB | .993 | -33.79 | (1) |
| 26 | Dakota Gas Well | PC | 32N-10W-01ADB | .999 | -32.86 | (2) |
| 27 | Animas River | Seep | 32N-09W-06BCA | .986 | -33.26 | (2) |
| 28 | Dakota Gas Well | PC | 32N-09W-06BCA | 1.00 | -32.79 | (1) |
| | Dakota Gas Well | IC | 32N-09W-06BCA | .998 | -32.18 | (2) |
| | Dakota Gas Well | SC | 32N-09W-06BCA | .990 | -32.21 | (2) |
| 29 | Junior Bonds | Soil seep | 32N-09W-06BCA | .990 | -37.84 | (1) |
| 30 | Pictured Cliffs Gas Well | PC | 32N-09W-06DCA | .873 | -42.98 | (2) |
| 31 | Dakota Gas Well | Casing soil | 32N-10W-12DCA | .972 | -41.01 | (1) |
| | Dakota Gas Well | PC | 32N-10W-12DCA | .998 | -32.62 | (1) |
| 32 | Robert Kinslow | Water | 32N-09W-18CBB | .988 | -52.15 | (1) |

**Table 4.** Gas-wetness fractions and methane-carbon-isotope ratios for selected gas samples from ground water, soil and river seeps, soil adjacent to gas-well casings, and from surface, intermediate, and, production casings of gas wells --Continued

| Site number (see plate 3) | Water well or land owner, gas-well formation, or site description | Gas source | Land-net location | Gas wetness, W | $\partial^{13}C_1$ (‰) | Data source |
|---|---|---|---|---|---|---|
| | | | **CEDAR HILL ZONE** | | | |
| 33 | Patricia Johnson | Water | 32N-10W-10CDD | 1.00 | -67.71 | ([1]) |
| 34 | Mesaverde Gas Well | SC | 32N-10W-28BCA | .997 | -43.43 | ([2]) |
| | Mesaverde Gas Well | CPW | 32N-10W-28BCA | .997 | -43.64 | ([2]) |
| 35 | Mesaverde Gas Well | CPW | 32N-10W-28ABD | .882 | -41.00 | ([2]) |
| 36 | Mesaverde Gas Well | SC | 32N-10W-27BAD | .993 | -43.28 | ([2]) |
| 37 | Fruitland Gas Well | PC | 32N-10W-33BAC | .997 | -43.23 | ([2]) |
| 38 | Fruitland Gas Well | PC | 32N-10W-33ACA | .997 | -43.09 | ([1]) |
| 39 | Lanier Clark | Soil seep | 32N-10W-34BCB | .995 | -43.99 | ([1]) |
| 40 | Mesaverde Gas Well | PC | 32N-10W-34BAD | .870 | -41.11 | ([1]) |
| 41 | Dakota Gas Well | Casing soil | 32N-10W-34BAD | .907 | -38.61 | ([1]) |
| | Dakota Gas Well | PC | 32N-10W-34BAD | .993 | -42.62 | ([1]) |
| 42 | Fruitland Coal Gas Well | PC | 32N-10W-32CAC | .997 | -43.29 | ([2]) |
| 43 | Mesaverde Gas Well | Casing soil | 32N-10W-32DBD | .993 | -43.81 | ([1]) |
| | Mesaverde Gas Well | PC | 32N-10W-32DBD | .858 | -41.75 | ([1]) |
| 44 | Benson Leeper | Soil seep | 31N-10W-05AAA | .992 | -40.98 | ([1]) |
| 45 | Charles Head | Water | 31N-10W-04AAA | .972 | -40.82 | ([1]) |
| 46 | Pictured Cliffs Gas Well | PC | 31N-10W-04ABD | .976 | -42.42 | ([1]) |
| 47 | Mesaverde Gas Well | PC | 31N-10W-04ABD | .865 | -41.55 | ([1]) |
| 48 | Dutchman Hills | Water | 31N-10W-04BDA | .984 | -38.11 | ([1]) |
| 49 | Mesaverde Gas Well | CPW soil | 31N-10W-03BCD | .992 | -43.86 | ([1]) |
| | Mesaverde Gas Well | PC | 31N-10W-03BCD | .984 | -42.69 | ([1]) |
| 50 | Mesaverde Gas Well | PC | 31N-10W-05ADB | .859 | -41.82 | ([1]) |
| 51 | Mesaverde Gas Well | CPW | 31N-10W-04BCD | .956 | -41.64 | ([2]) |
| 52 | Mesaverde Gas Well | Casing soil | 31N-10W-04DBD | .936 | -40.57 | ([1]) |
| | Mesaverde Gas Well | PC | 31N-10W-04DBD | .901 | -42.03 | ([1]) |
| 53 | Pictured Cliffs Gas Well | SC | 31N-10W-03CCA | .984 | -42.63 | ([2]) |
| 54 | Gas Pipeline | CPW | 31N-10W-05DAC | .905 | -41.36 | ([2]) |
| 55 | Pictured Cliffs Gas Well | SC | 31N-10W-09BAC | .940 | -41.39 | ([2]) |
| 56 | Mesaverde Gas Well | Casing soil | 31N-10W-07CAC | .860 | -34.82 | ([1]) |
| | Mesaverde Gas Well | PC | 31N-10W-07CAC | .843 | -41.80 | ([1]) |
| | | | **AZTEC ZONE** | | | |
| 57 | Pictured Cliffs Gas Well | Casing soil | 31N-11W-25BAC | .899 | -40.31 | ([1]) |
| | Pictured Cliffs Gas Well | PC | 31N-11W-25BAC | .899 | -40.27 | ([1]) |
| 58 | Mesaverde Gas Well | PC | 31N-11W-25BCA | .853 | -42.19 | ([1]) |
| 59 | Fruitland Coals Gas Well | PC | 31N-11W-36CBD | .904 | -41.95 | ([1]) |
| 60 | Pictured Cliffs Gas Well | Casing soil | 30N-11W-03BBD | .881 | -39.25 | ([1]) |
| | Pictured Cliffs Gas Well | PC | 30N-11W-03BBD | .882 | -39.72 | ([1]) |

[1]Chafin and others (1993)

[2]Dudley Rice, U.S. Geological Survey, written commun., 1991

ble mechanical sources for the sampled gas. This gas well has a production casing to a depth of 4,383 ft and a casing liner hung from 4,158 ft to total depth at 8,725 ft. Two packers separate the casing-and-liner string into the three producing intervals, which allows the possibility of Mesaverde gas leaking past the upper packer. Furthermore, construction records indicate that the casing annulus is not cemented along the lower Kirtland Shale, Fruitland Formation, and Pictured Cliffs Sandstone and to the depth where the casing liner joins the production casing; this open annulus possibly allows gas from one or more of the exposed formations to flow into the casing above the upper packer (at a depth of 6,252 ft) through the short cement junction between the casing and liner. The sampled gas closely resembles the previously described gas sample from sandstones in the Fruitland Formation.

NMOCD records indicate that three wells have produced gas from the Nacimiento Formation in the New Mexico part of the San Juan Basin. One well is about 65 mi southeast of Aztec, New Mexico, at 24N-02W-12 and during 1980-81 produced small volumes of wet gas (W = 0.914) from a 15-ft-thick sandstone reservoir at a depth of 2,380 ft. The gas composition resembles that of gas from wells completed in the Pictured Cliffs Sandstone a few miles away, as reported by Rice (1983, p. 1208). The well producing gas from the Nacimiento Formation was plugged back from the Pictured Cliffs Sandstone and is located in a field of abandoned gas wells. Rice and others (1989, p. 605) show $R_0$ values for coals in the Fruitland Formation in this area to be about 0.5 percent, implying that the gas in the Nacimiento Formation (about 1,000 ft higher than coals in the Fruitland Formation) probably was leaked thermogenic gas because it is too wet to be biogenic. However, the possibility that localized deposits of humic organic matter in the Nacimiento Formation generated relatively immature thermogenic gas cannot be eliminated.

Two gas wells completed in the Nacimiento Formation are recorded in the vicinity of the study area. A well at 31N-10W-14, about 3 mi southeast of Cedar Hill, produced small volumes of wet gas (W = 0.882) and light oil from a 12-ft-thick sandstone at a depth of 978 ft. The drillhole reportedly blew out at 990 ft while being drilled in 1975, indicating overpressuring, and was drilled to a total depth of 3,195 ft and completed dually in the Nacimiento Formation and Pictured Cliffs Sandstone. Overpressuring can indicate gas transfer from a deeper stratum with higher gas pressures. The large sulfate concentration (6,300 mg/L) of the associated water from the Nacimiento Formation should have destroyed indigenous methane by oxidation over geologic time. Rice (1983, p. 1209) and Chafin and others (1993, p. 83) describe gas samples from wells in the Mesaverde Group in the vicinity that are similar in composition to the gas produced from this well (at 31N-10W-14) in the Nacimiento Formation. Furthermore, Rice (1983, p. 1215) reports that gas wells completed in the Mesaverde Group in the vicinity locally produce oil. Fassett (1978, p. 59) assumed that this gas well in the Nacimiento Formation was charged by migration from deeper gas-bearing formations because the Nacimiento Formation consists of continental deposits, which (in 1978) had produced no hydrocarbons anywhere else in the basin.

Another gas well in the Nacimiento Formation, at 32N-11W-34 about 5 mi west of Cedar Hill, reportedly was drilled into an overpressured sand at a depth of 725 ft in 1975 and showed a rapid decline in its relatively small gas yield after two years of production. NMOCD records indicate the subsequent plugging of two older defective gas wells within a 0.5 mi radius, suggesting possible origins for this gas. No gas analysis is available for this well in the Nacimiento Formation, and no oil was produced. Despite evidence that gas produced from the Nacimiento Formation at 31N-10W-14 and 32N-11W-34 probably leaked from gas wells completed in deeper formations, the possibility that indigenous gas was produced from localized deposits of humic organic matter at a relatively immature thermogenic stage cannot be discounted. According to the description of such gas documented by Galimov (1988, p. 91), humus-derived gas should have $\partial^{13}C_1$ values less than or equal to -46‰.

Several other reports of relatively shallow gas in the vicinity of the study area assist in characterizing the maturity of gases in the near-surface Nacimiento Formation. Humic organic matter produces an early condensate at a maturity less than that of the main stage of oil formation (Galimov, 1988, p. 91). Oldaker (1991, p. 4) reports that at Aztec in 1921, a gas well was drilled into the Farmington Sandstone of the Kirtland Shale and encountered a large flow of gas with condensate at a depth of 990 ft and recorded oil at 1,190 to 1,270 ft. Therefore, this information indicates that oil formation began at a depth greater than 1,100 ft at Aztec. This conclusion is consistent with an $R_0$ value of about 0.65 percent for coals in the Fruitland Formation about 1,000 ft deeper (Rice and others, 1989, p. 605, fig. 5). The oil-production stage is associated with $R_0$ values greater than about 0.6 percent. The driller's log for a gas well drilled in 1937 at 33N-09W-31CCD at Bondad (COGCC records) records gas shows at depths of 1,010, 1,206, 1,806, 1,865, 1,945, and 2,240 ft and minor oil shows at 1,285 and 1,979 ft. The log listed small coal seams at 367 and 1,603 ft but did not indicate gas associated with the coal. The uppermost gas shows (probably to 1,945 ft) were in the Kirtland Shale, which indicates that at this site, the Nacimiento Formation was barren of gas in 1937. The oil at 1,285 and 1,979 ft indicate that the early or peak oil-generation stages occurred in this interval and that any gas indigenous to the overlying Nacimiento Formation should be biogenic or earliest mature thermogenic gas having $\partial^{13}C_1$ values less than -50‰. Because thermal maturities of coals in the Fruitland Formation are approximately equal ($R_o$ values of 1.0 to 1.1 percent) beneath the Colorado reach of the study area (Rice and others, 1989, p. 605, fig. 5), it is reasonable to assume that the thermal maturity of any indigenous gas in the Nacimiento and Animas Formations beneath the study area north of Bondad also are approximately equal. Therefore, any site in the Nacimiento Formation is probably barren of gas (as at 33N-09W-31CCD), yields indigenous gas that is biogenic or earliest thermogenic ($\partial^{13}C_1$ less than -50‰), or yields thermogenic gas that leaked from a deeper formation. The 300-ft-deep Weekly water well at 34N-09W-07ADC (site 2 in table 4) has dissolved gas that exhibits a $\partial^{13}C_1$ value of -59.66‰ and that appears to be biogenic or earliest thermogenic gas.

The discovery of volcaniclastic deposits of Oligocene age provides new information about the late Tertiary burial history of the San Juan Basin that can be used in conjunction with hydrocarbon-maturity calculations to show that substantial amounts of indigenous thermogenic gas probably never developed in the Animas and Nacimiento Formations beneath the study area. The presence of these volcaniclastic deposits in the Animas River valley and at other locations in the northern San Juan Basin indicates that the Animas, Nacimiento, and San Jose Formations had been eroded to their present thicknesses before burial by volcaniclastic deposits and that post-Oligocene erosion rates were smaller than those assumed by previous investigators.

The maximum thickness of the volcaniclastic deposits over the northern San Juan Basin at about the end of the Oligocene Epoch, when the most voluminous phases of volcanic eruptions ended, is not known, due to subsequent erosion. The Shiprock volcanic plug near Shiprock, New Mexico, was intruded through volcaniclastic deposits near the end of the Oligocene Epoch. The plug currently stands about 1,700 ft above the surrounding plain, which can be assumed to closely represent the pre-volcanic erosional surface because of the integrated terraces of the nearby San Juan River to the north, the Animas River to the northeast, and the Chaco River to the east and south (fig. 2). Therefore, 1,700 ft is a minimum estimate of the thickness of volcaniclastics at the plug. Delaney (1987, p. 412) reported airfall deposits in the plug. Assuming that the airfall deposits could deposit no deeper than 300 ft below the top of the volcaniclastic overburden, 2,000 ft is an estimate for maximum thickness for volcaniclastic deposits at the plug. Based on present topography, the thickness would have been about 2,500 ft over the San Juan River at Shiprock, New Mexico. A volcaniclastic thickness of 3,000 ft at maximum burial will be assumed for the Animas River valley.

Burial depths can be used to estimate concomitant geothermal gradients and thermal maturities of buried hydrocarbons and to show that substantial indigenous thermogenic gas probably did not form in the Animas and Nacimiento Formations. Waples (1980) described the use of the Lopatin time-temperature index (TTI) to calculate thermal maturities of hydrocarbons in sediments. TTI's are calculated by reconstructing the burial and geothermal-gradient histories for a source formation and integrating a temperature function over time. TTI values are related to hydrocarbon maturities by the assumption that the rate at which kerogen is converted to hydrocarbons progresses linearly with time and exponentially with temperature. TTI calculations assume that reaction rates double with every 10°C (18°F) increase in temperature. Therefore, because temperatures usually increase with depth, TTI values usually increase with depth, signifying greater potential hydrocarbon maturities with depth. Accordingly, steeper geothermal gradients are associated with steeper hydrocarbon-maturity profiles.

Rice (1983) used TTI calculations to conclude a maximum temperature of 320 to 360°F for coals in the Fruitland Formation at a current depth of about 2,200 ft at 34N-08W-11, about 11 mi southeast of Durango. At this site, coals in the Fruitland Formation have an $R_o$ value of 1.45 percent; Waples (1980, p. 291) reports a TTI of about 250 corresponding to this $R_o$ value. Rice (1983) assumed that 6,000 ft of rocks of Cretaceous through early Tertiary age and 4,000 ft of volcanic rocks of Oligocene age covered the coals in the Fruitland Formation at maximum burial during the Oligocene Epoch, resulting in geothermal gradients of 2.6 to 3.0°F/100 ft (after correcting for surface temperature). Bond (1984) assumed a maximum burial of about 8,700 ft for coals in the Fruitland Formation, including about 1,600 ft of volcaniclastic deposits of Oligocene age, for this same site. He concluded that the assumed peak geothermal gradient of 3.1°F/100 ft caused coal temperatures to reach about 320°F and caused oil-generating temperatures in the Animas Formation. However, assuming only 2,300 ft of volcaniclastic deposits over present overburden (because the site is about 700 ft higher than the Animas River valley due west), a maximum temperature of 320°F implies an average geothermal gradient of 5.8°F/100 ft at maximum burial. Halving the TTI value for every 18°F decrease results in a TTI value of 9 for the base of the Animas Formation, about 1,500 ft above the coals in the Fruitland Formation. Waples (1980, p. 921) associated oil generation with a TTI value equal to or greater than 15. Therefore, burial depth indicates that the Animas Formation probably never reached the oil-generation stage at this site and that the Animas and Nacimiento Formations are not likely to have generated oil or substantial thermogenic gas beneath the Animas River valley, where coals in the Fruitland Formation are less mature (maximum $R_0$ = 1.1 percent). This calculated TTI value is maximum (for the assumptions involved) because, as reported by Bond (1984, p. 433), the onset of overpressuring in the Fruitland Formation and Kirtland Shale during the Oligocene Epoch created a loss of thermal conductivity and a corresponding increase in paleogeothermal gradient to about 2.0°F/100 ft greater than that of overlying rocks. This effect is substantiated by modern geothermal gradients at Bondad, where the gradient through the overpressured Fruitland Formation and the lower Kirtland Shale averages 3.3°F/100 ft, whereas the gradient in overlying rocks averages 2.2°F/100 ft (Reiter and Mansure, 1983, p. 242, fig. 2b). This effect implies smaller TTI values than that calculated for the base of the Animas Formation or would allow the assumption of greater thickness for volcaniclastic overburden. Therefore, a revised maximum burial depth indicates that substantial indigenous thermogenic gas probably did not form in the Animas and Nacimiento Formation.

## Analysis of Specific Gas Samples

In the analysis of the geochemistry of specific gas samples from water, soil, and gas-well casings in the study area, six zones were delineated to account for local variations in production-gas compositions. This approach was necessary because of the relatively systematic variation of the geochemistry of produced gases along the north-south axis of the study area. The six zones (pl. 3) are: (1) Northern, (2) Sunnyside Mesa, (3) North Bondad, (4) South Bondad, (5) Cedar Hill, and (6) Aztec.

### Northern Zone

Plots of $\partial^{13}C_1$ values and wetness fractions for gas samples collected in the Northern zone (table 4; pl. 3) are shown in figure 14. The $\partial^{13}C_1$ value (-59.66‰) and the wetness value of 1.00 for the Charles Weekly water sample (site 2) indicates that the dissolved gas is biogenic. The $\partial^{13}C_1$ value (-37.16‰) for the Ollier water sample (site 5) indicates a thermogenic source. Various mixtures of gases from the Dakota Sandstone, Mesaverde Group, and Fruitland Formation or oxidation of coal-bed gas from the Fruitland Formation could account for this gas composition.

### Sunnyside Mesa Zone

Plots of $\partial^{13}C_1$ values and wetness fractions for gas samples collected in the Sunnyside Mesa zone (table 4; pl. 3) are shown in figure 15. The soil-gas sample collected adjacent to the casing of the Mesaverde gas well at 33N-10W-01CDA (site 7) has a $\partial^{13}C_1$ value similar to gas from coals in the Fruitland Formation (Fruitland coal gas well, site 8). COGCC records indicate that this gas well had a surface-casing pressure of 37 lb/in$^2$ on April 15, 1991, indicating that the soil gas probably migrated from the surface casing of this gas well.

The wetness fraction and $\partial^{13}C_1$ value for gas from the Obery water sample (site 9) are most similar to those values for gas from the Dakota gas well at 33N-10W-24AAC (site 10), which is 0.17 mi to the south. During August 1990, this gas well was remediated to repair a casing leak at a depth of 26 ft, which caused a surface-casing pressure of 2,000 lb/in$^2$ (James Lovato, U.S. Bureau of Land Management, written commun., 1991). Water sampled from the Obery well on August 20, 1990, while this gas well was being repaired, had a dissolved-methane concentration of 19 mg/L. Following repair, on November 15, 1990, the dissolved-methane concentration was 9.0 mg/L. The dissolved-methane concentration declined further to 4.5 mg/L on March 6, 1991. Slight oxidation of methane apparently is indicated by the 2.16‰ difference in $\partial^{13}C_1$ values for the Obery well water (-30.73‰) and the Dakota gas well (-32.89‰).

### North Bondad Zone

Plots of $\partial^{13}C_1$ values and wetness fractions for gas samples collected in the North Bondad zone

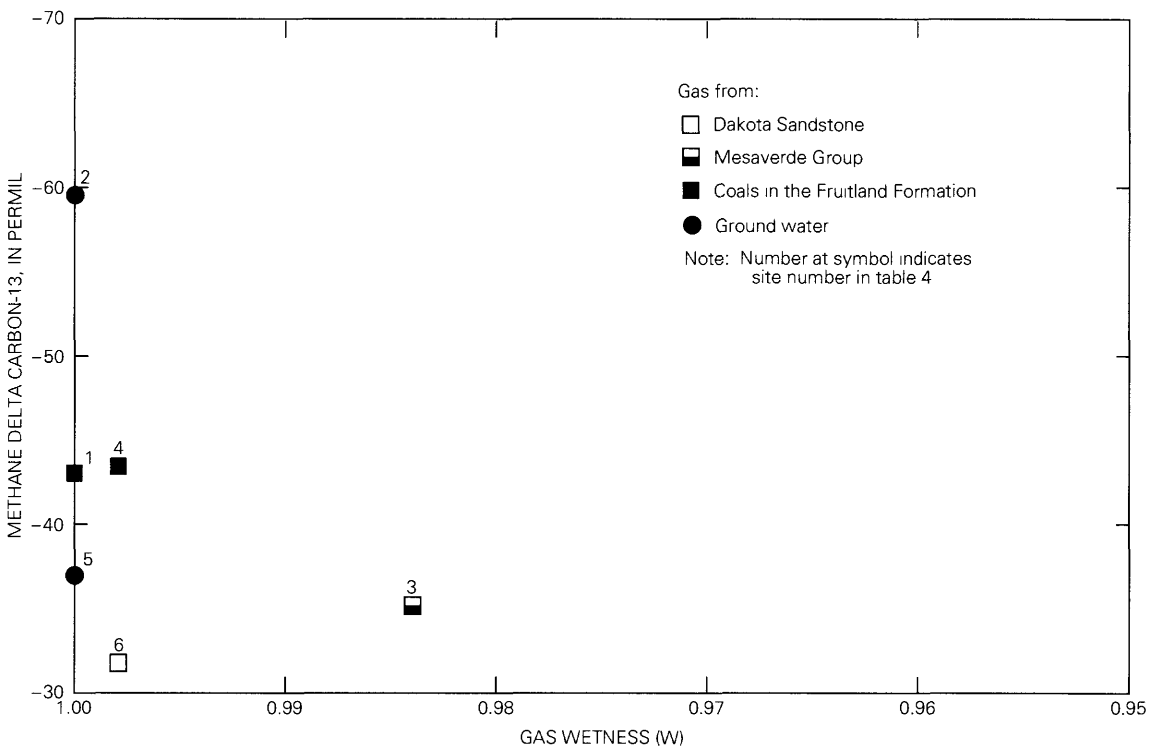



**Figure 14.** Values for methane delta carbon-13 and gas wetness for gas samples collected in the Northern zone.

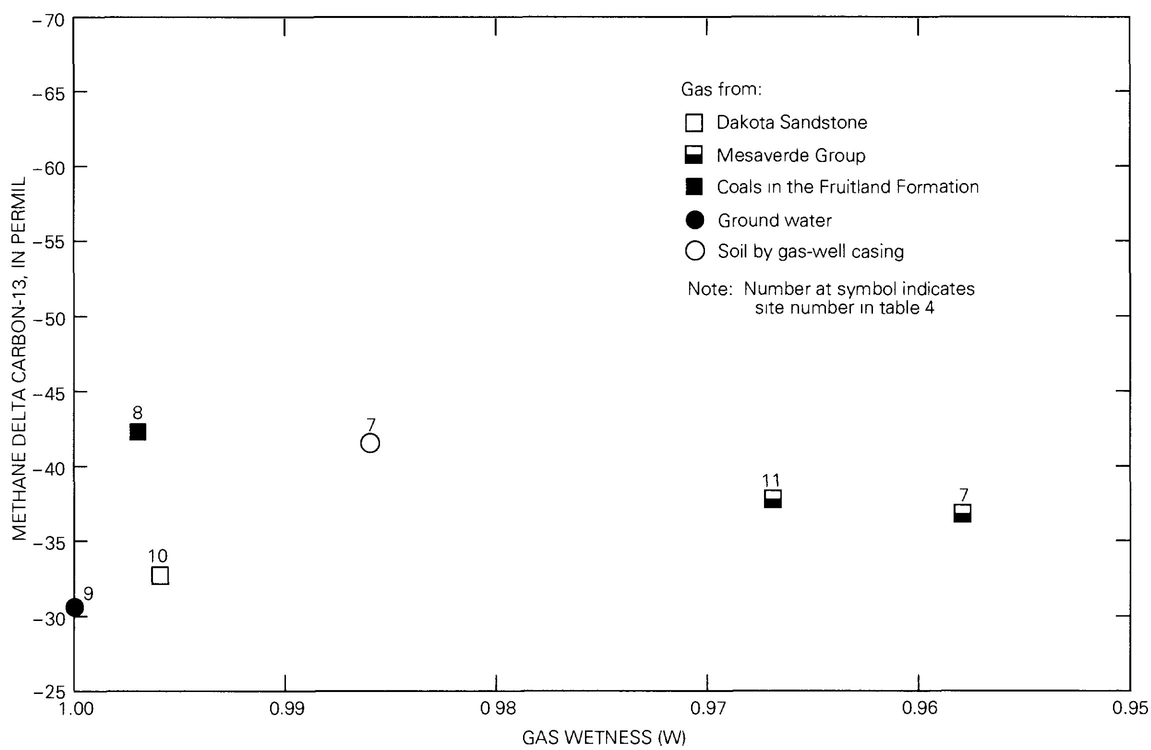



**Figure 15.** Values for methane delta carbon-13 and gas wetness for gas samples collected in the Sunnyside Mesa zone.

(table 4; pl. 3) are shown in figure 16. The $\partial^{13}C_1$ value (-41.96‰) for gas from the Haneman water well (site 13) plots in the narrow range of values for coal gases in the Fruitland Formation (site 8 to the north, -42.37‰, and site 16 to the south, -41.91‰). The smaller wetness value (0.982) for the dissolved gas in the Haneman well compared to the wetness values for the coal-bed gases (>0.99) appears to indicate that the dissolved gas underwent slight aging distillation, which caused a relative enrichment in $C_{2+}$ hydrocarbons.

Soil gas collected adjacent to the casing of a Mesaverde gas well at 33N-10W-25ABD (site 14) has a $\partial^{13}C_1$ value that is 2.27‰ heavier than the value for the Mesaverde gas from that gas well, and the soil gas is substantially more enriched in $C_{2+}$ hydrocarbons. A leak in the wellhead of this well permitted gas to leak from the production casing into the surface casing, which caused a surface-casing pressure of 108 lb/in$^2$ on March 21, 1991 (Mark Weems, COGCC, written commun., 1991). On August 14, 1991, COGCC collected gas samples from the production tubing, surface casing, and from a cathodic-protection well that is located about 150 ft northwest of the gas well and was flowing gas and water when sampled. The molecular ($C_1$ - $C_5$) compositions of the gas samples (Mark Weems, COGCC, written commun., 1991) were virtually identical. The mechanism for $C_{2+}$ enrichment of the soil gas is not known.

The similarity in isotopic compositions of gas from the Gamble water well (site 15) and produced Mesaverde gas from site 14, which is 0.23 mi to the northwest, suggests the Mesaverde Group as a probable source for the gas in the water well. A slightly heavier $\partial^{13}C_1$ value for the water sample (1.18 ‰) suggests slight oxidation, and the greater wetness fraction for the gas from the water suggests methane enrichment during horizontal migration.

### South Bondad Zone

Plots of $\partial^{13}C_1$ values and wetness fractions for gas samples collected in the South Bondad zone (table 4; pl. 3) are shown in figure 17. Gases from the Kloepfer water well (site 17) and soil adjacent to the Dakota gas well at 33N-10W-36DAC (site 18) are similar in isotopic composition to coal-bed-gas samples

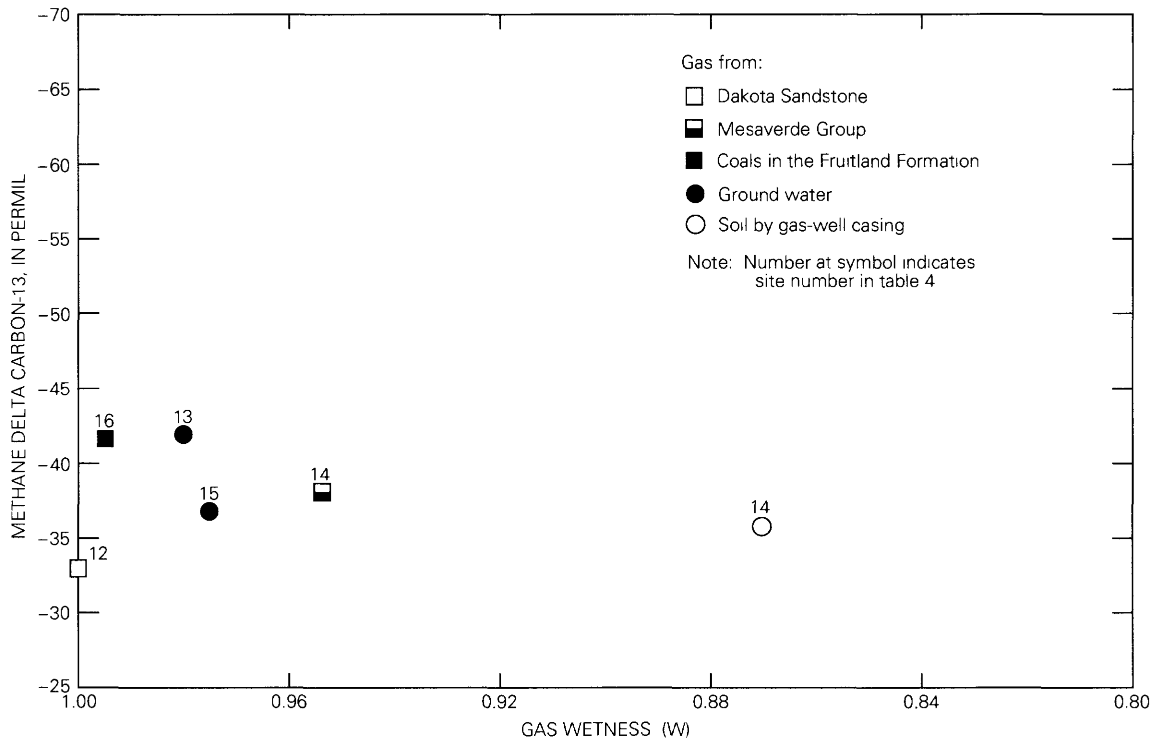



**Figure 16.** Values for methane delta carbon-13 and gas wetness for gas samples collected in the North Bondad zone.

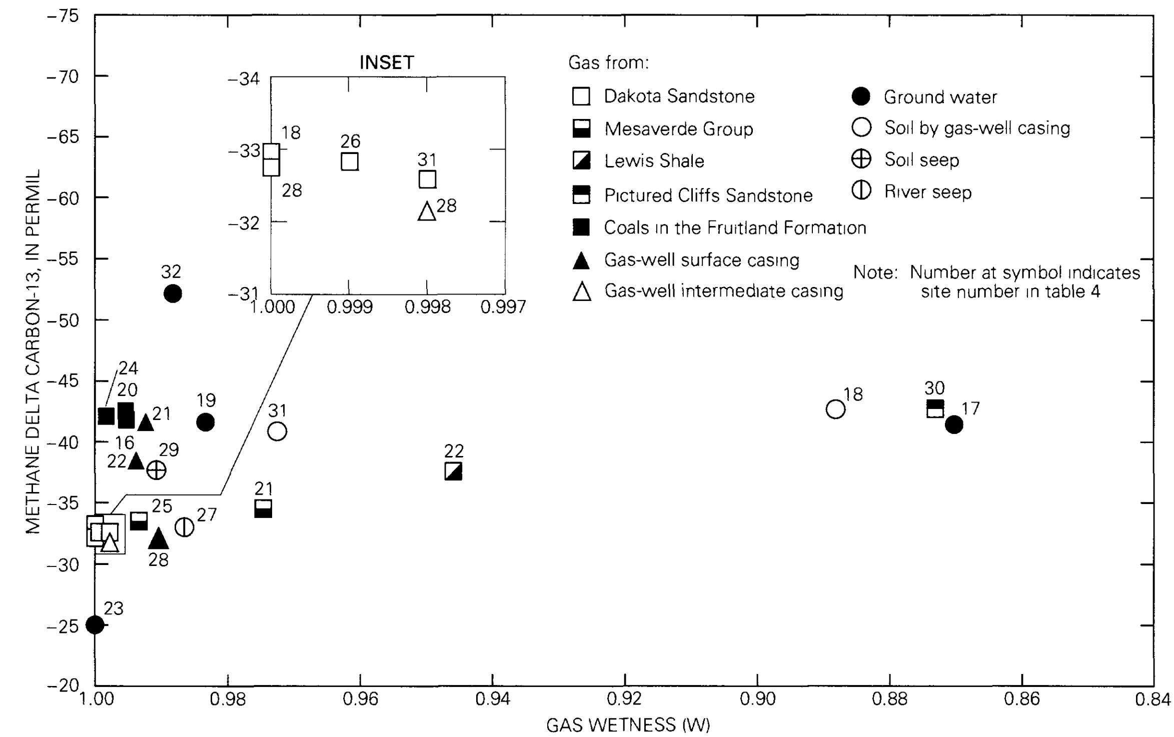



**Figure 17.** Values for methane delta carbon-13 and gas wetness for gas samples collected in the South Bondad zone.

collected from Fruitland gas wells at 33N-10W-25DDB (site 16), 33N-09W-31CCD (site 20) and 32N-10W-01AAC (site 24). However, other factors and the substantially smaller wetness fractions for gases from the water at site 17 and the soil adjacent to the gas well at site 18 compared to wetness fractions for the coal-bed gases indicate that the overlying Kirtland Shale is a more likely source. The annulus of the gas well at site 18 probably was open to the Kirtland Shale. Gas-well construction data (COGCC records) indicate that the top of cement in the annulus was at about 1,780 ft below land surface (in the lower Kirtland Shale), assuming a 75-percent excess for required cement volume. However, Beckstrom and Boyer (1991, p. 376) state that in the Cedar Hill area 200-percent excess-cement volumes were required to fill annular spaces above the Fruitland Formation. Use of this greater cement requirement would result in a cement top at about 2,250 ft below the land surface, about 110 ft below the top of the Fruitland Formation. The 1937 driller's log for the abandoned gas well at site 20, 0.4 mi southeast of site 18, lists Kirtland Shale gas shows at 1,010 and 1,806 ft, and a strong blow of Kirtland gas at 1,865 ft. U.S. Bureau of Land Management records report an analysis for gas from the Farmington Sandstone of the Kirtland Shale (W = 0.884) near Aztec, that closely resembles the analysis for the soil gas from site 18 (W = 0.888) and has a similar wetness as the dissolved gas from site 17 (W = 0.870).

COGCC records indicate that the cathodic-protection well near the gas well at site 18 was cemented during February 1989 to stop the flow of salty water being driven upward by gas flow. The flow of gas and water from this cathodic-protection well indicates a nearby gas supply, suggesting that the annulus of the Dakota gas well at site 18 may be part of a migration pathway for gas at sites 17 and 18. However, COGCC records indicate that the next nearest gas well (a Mesaverde well at 33N-10W-36DBD), 0.20 mi south of site 17 and 0.15 mi northwest of site 18, also has an uncemented annulus extending into the Kirtland Shale. This annulus may provide another conduit for gas from the Kirtland Shale. The unique composition of gas from site 17 possibly results mostly from volatilization of methane from the near-surface gas body (aging distillation) and oxidation during the interval between cementing of the cathodic-protection well at site 18 in February 1989 and sampling of site 17 during November 1990.

The $\partial^{13}C_1$ value for gas from the Weston water well (site 19) closely resembles that of gas from an abandoned gas well (site 20), which is located about 0.10 mi southeast. This gas well has been open to the Nacimiento Formation since 1937, when it was drilled into coals in the Fruitland Formation. The $\partial^{13}C_1$ values for gases from site 20 and the surface casing of the Mesaverde gas well at 32N-09W-06BBD (site 21), 0.27 mi to the south, also are similar. The 1.15‰ heavier $\partial^{13}C_1$ value for the latter site indicates the possibility of the oxidation of gas during migration through sandstones.

$\partial^{13}C_1$ values for gas seeping from the Animas River at site 27 (-33.26‰), gas from the intermediate casing of site 28 (-32.18‰), and gas from the surface casing of site 28 (-32.21‰) agree well with the value for Dakota Sandstone production gas from site 28 (-32.79‰), which is about 500 ft south of the river seep. The first three of these samples were collected by COGCC in July 1989, and the gas well at site 28 had casings cemented during November 1990.

Gas from the Bonds soil seep (site 29) has a $\partial^{13}C_1$ value (-37.84‰) that closely agrees with the $\partial^{13}C_1$ value for gas produced from the Lewis Shale gas well at site 22 (-37.58‰), 0.28 mi to the north. Furthermore, gas collected from the surface casing of the Lewis Shale gas well during July 1989 has a $\partial^{13}C_1$ value (-38.52‰) that agrees well with that value from the soil seep. COGCC records indicate that the Lewis Shale gas well at site 22 had a *bradenhead* pressure of 140 lbs/in$^2$ in April 1992 and that in October 1992 the operator submitted plans to plug this gas well.

The exceptionally heavy $\partial^{13}C_1$ value (-25.20‰) for gas from the Walter water well (site 23) indicates substantial oxidation of thermogenic gas. Information is not available to indicate a more specific source formation.

Gas collected from soil adjacent to the casing of the Dakota gas well at 32N-10W-12DCA (site 31) has a $\partial^{13}C_1$ value similar to those values for Fruitland coal-bed-gas samples. On December 10, 1990, when the soil-gas-methane concentrations was measured at 80 mg/L$_g$, the surface-casing pressure was 160 lb/in$^2$. When soil gas and production gas were collected from this well on March 5, 1991, the soil-gas-methane concentration was 350 mg/L$_g$, and the surface-casing pressure was 560 lb/in$^2$. COGCC records indicate that this pressure had increased to 880 lb/in$^2$ on July 30, 1991, and that gas collected from the surface casing then had a wetness value of 0.915. A temperature log indicated that the annular space of this gas well was not cemented above a depth of 2,550 ft, thereby leaving a conduit from the upper 150 ft of the Fruitland Formation and all of the Kirtland Shale to the Nacimiento Formation. The wetness of the surface-casing gas suggests a source from sandstones of the upper Fruitland Formation or the Kirtland Shale, or both.

Gas from the Kinslow water well (site 32) has a $\partial^{13}C_1$ value that in combination with a large wetness fraction indicates mostly biogenic gas.

### Cedar Hill Zone

Plots of $\partial^{13}C_1$ values and wetness fractions for gas samples collected from gas-producing formations and from the shallow subsurface environment in the Cedar Hill zone (table 4; pl. 3) are shown in figure 18. Except for site 33, the $\partial^{13}C_1$ values for all samples are greater than -44‰, which indicates that gas collected from the shallow subsurface environment (except at site 33) is thermogenic in origin and came from gas-bearing formations beneath the study area.

Gas from the Johnson water well (site 33) has the lightest $\partial^{13}C_1$ value (-67.71‰) for samples collected for this study and indicates a biogenic source. Gas collected from the soil adjacent to the casings of the Dakota gas well at 32N-10W-34BAD (site 41) and the Mesaverde gas well at 31N-10W-07CAC (site 56) and gas collected from the Dutchman Hills water well (site 48) have $\partial^{13}C_1$ values that are substantially heavier than that for the heaviest thermogenic production sample collected in the zone (-41.11‰). These gases are thermogenic gases that underwent oxidation of methane near the land surface. Information is not available to indicate more specific source formations for these thermogenic samples.

Six samples have $\partial^{13}C_1$ values and wetness fractions that are similar to those for gas from coals in the Fruitland Formation in this zone (sites 37, 38, and 42). These samples are from the surface casing and cathodic-protection well of the Mesaverde gas well at 32N-10W-28BCA (site 34), the surface casing of the Mesaverde gas well at 32N-10W-27BAD (site 36), the Clark soil seep (site 39), soil by the casing of the Mesaverde gas well at 32N-10W-32DBD (site 43), and soil by the cathodic-protection well of the Mesaverde gas well at 31N-10W-03BCD (site 49). The $\partial^{13}C_1$ values for these samples are within the range -43.28 to -43.99‰, and wetness fractions exceed 0.99. NMOCD records indicate that the gas well at site 49 was

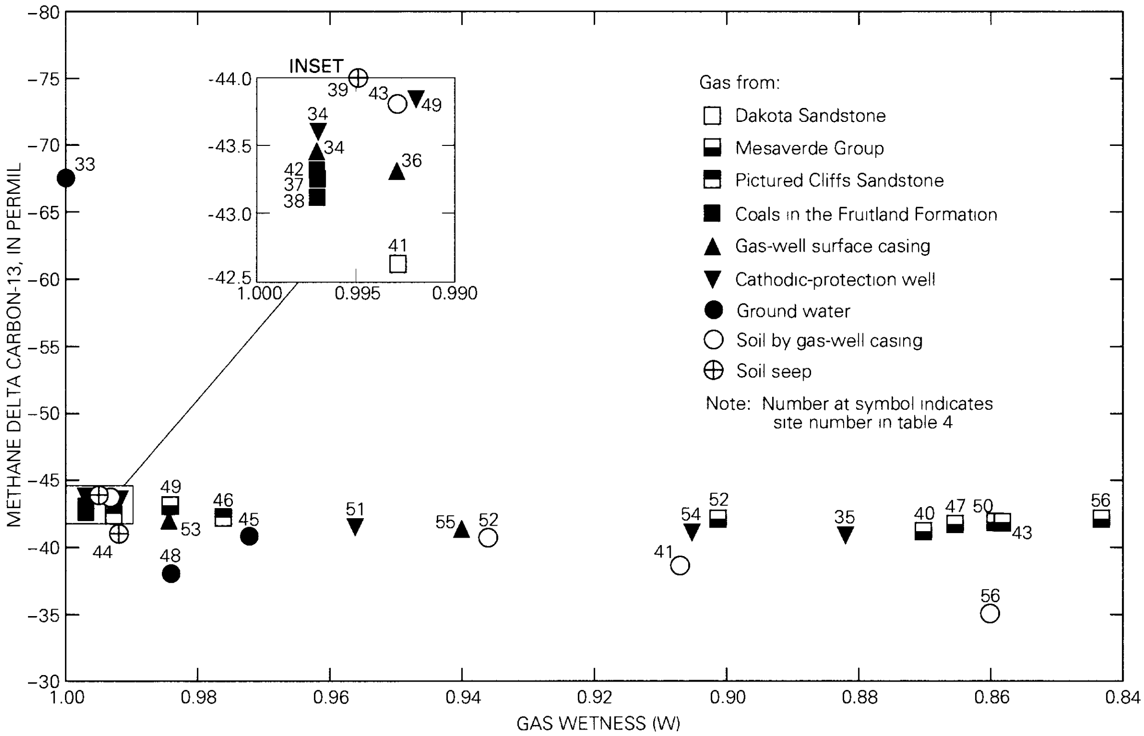



**Figure 18.** Values for methane delta carbon-13 and gas wetness for gas samples collected in the Cedar Hill Zone.

cemented across the coals in the Fruitland Formation in May 1990, and that during 1990 numerous gas wells in the Cedar Hill zone were plugged and abandoned or had coals in the Fruitland Formation cemented to prevent upward migration of coal-bed gas.

Gas collected from the cathodic-protection well of the Mesaverde gas well at 32N-10W-28ABD (site 35) has similar wetness and $\partial^{13}C_1$ values as does Mesaverde gas from the gas well at 32N-10W-34BAD (site 40), located about 1 mi to the southeast. NMOCD records indicate that site 35 was plugged and abandoned in May 1990 after NMOCD directed that a casing failure be repaired.

Gas collected from the surface casing of the Pictured Cliffs gas well at 31N-10W-03CCA (site 53) has similar wetness and $\partial^{13}C_1$ values as does gas from the Pictured Cliffs gas well at 31N-10W-04ABD (site 46), located about 1 mi to the northwest. NMOCD records indicate that site 53 was plugged and abandoned in April 1990 after NMOCD directed remediation of a casing leak.

Areal distributions, pertinent gas-well information, and $\partial^{13}C_1$ values for most of the remaining near-surface samples in the Cedar Hill zone indicate that these samples probably contain gas from the Mesaverde Group. A plot of gas samples apparently from the Mesaverde Group and coals in the Fruitland Formation (with an expanded $\partial^{13}C_1$ scale) indicates the separate distributions of the two types of gas (fig. 19). The Mesaverde gas well at 32N-10W-34CDB (pl. 1) had a casing leak at a depth of 193 ft that was repaired in the fall of 1991 (Ernest Busch, NMOCD, oral commun., 1991). Although a $\partial^{13}C_1$ value for the production gas from this well is not available, $\partial^{13}C_1$ values for the two nearest Mesaverde gas wells, -41.11‰ at 32N-10W-34BAD (site 40) and -41.55‰ at 31N-10W-04ABD (site 47), average about -41.3‰. The $\partial^{13}C_1$ value for the Head water well (site 45, about 0.4 mi to the southwest of the Mesaverde gas well at 32N-10W-34CDB), -40.82‰, is similar to this average value (allowing for oxidation), which appears to indicate a Mesaverde source. Gas from the Leeper soil seep (site 44) has a $\partial^{13}C_1$ value (-40.98‰) that is slightly heavier than the value for production gas collected from the Mesaverde gas well at 31N-10W-05ADB, site 50 (located 0.35 mi

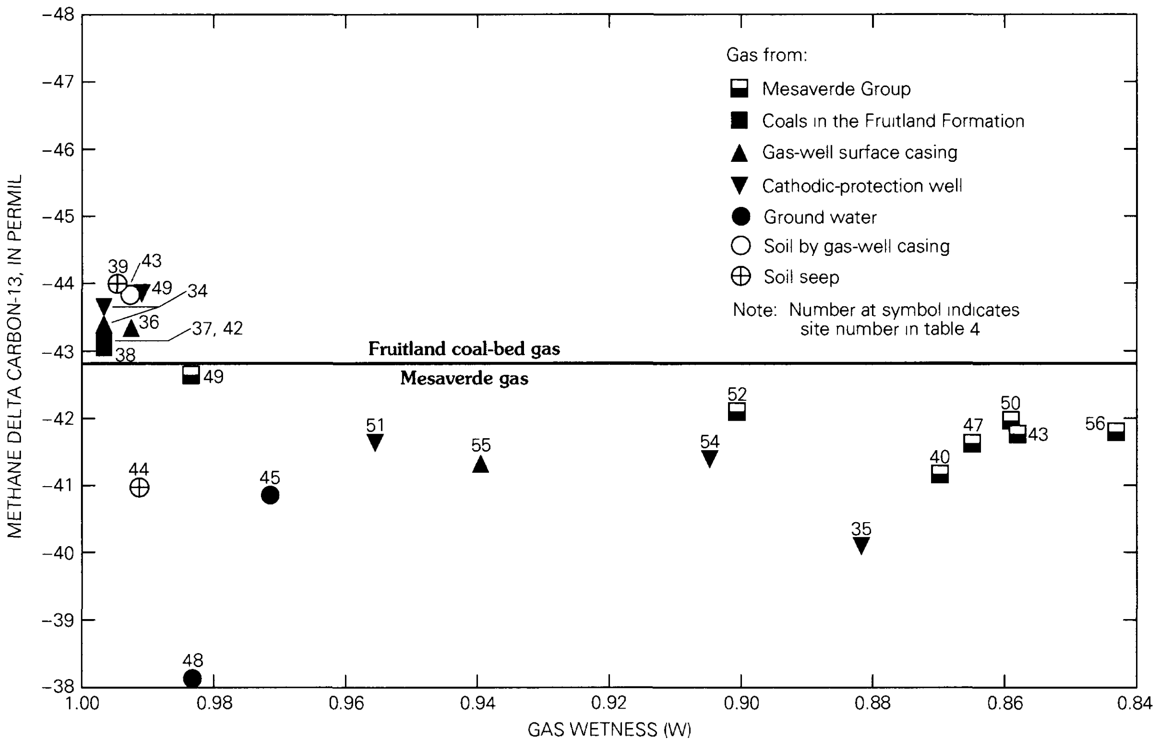



**Figure 19.** Values for methane delta carbon-13 and gas wetness for gas samples collected in the Cedar Hill zone from the Mesaverde Group and coals of the Fruitland Formation.

to the southwest of site 44), -41.82‰. This gas well indicated a pressure of at least 100 lb/in$^2$ in the intermediate casing on January 17, 1991. NMOCD records document that a production-casing leak and the surface casing of this gas well were cemented in 1976. When a coal-bed-gas well in the Fruitland Formation was drilled about 200 ft south of this gas well in October 1990, the drillhole blew out at a depth of 249 ft (Ernest Busch, NMOCD, personal commun., 1993). $\partial^{13}C_1$ values for gas collected from the cathodic-protection well of the Mesaverde gas well at 31N-10W-04BCD (site 51, located 0.40 mi to the east-southeast of site 50), -41.64‰, and the cathodic-protection well for a gas pipeline, site 54 (located 0.40 mi to the south-southeast of site 50), -41.36‰, are very similar to the $\partial^{13}C_1$ value for produced Mesaverde gas from site 50. The $\partial^{13}C_1$ value for gas from the surface casing of the Pictured Cliffs gas well at 31N-10W-09BAC (site 55), -41.39‰, agrees with those for produced Mesaverde gas. Gas in the water from the Dutchman Hills water well (site 48), although oxidized, possibly was derived from the Mesaverde Group, given the location of this water well among other sites apparently exhibiting Mesaverde gas. The $\partial^{13}C_1$ value for soil gas collected by the casing of the Mesaverde gas well at 31N-10W-04DBD (site 52) could indicate oxidized gas from the Mesaverde Group or the Pictured Cliffs Sandstone.

## Aztec Zone

Plots of $\partial^{13}C_1$ values and wetness fractions for gas samples collected from gas-producing formations and from the shallow subsurface environment in the Aztec zone (table 4; pl. 3) are shown in figure 20. Gas collected from the soil adjacent to the casings of Pictured Cliffs gas wells at 31N-11W-25BAC (site 57) and at 30N-11W-03BBD (site 60) have wetness fractions and $\partial^{13}C_1$ values that are almost identical to those compositions for gas from their respective producing formations. Furthermore, concentrations of hydrocarbon components for the pairs (Chafin and others, 1993) closely agree. NMOCD records indicate that site 57

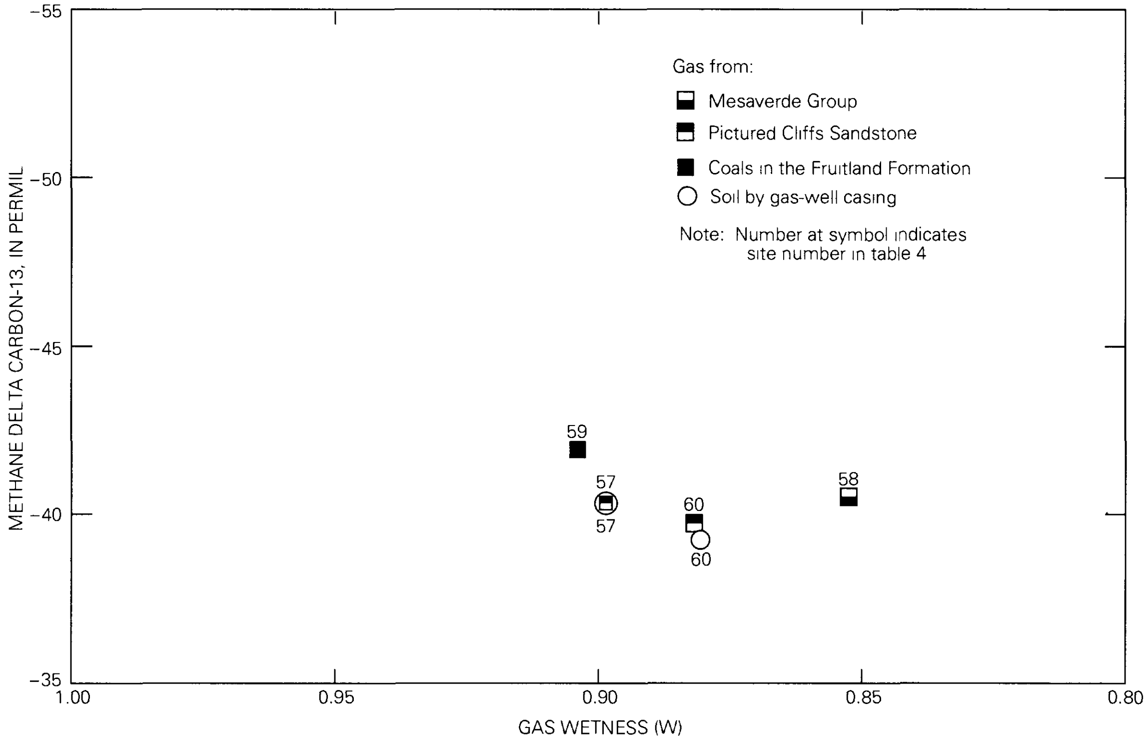



**Figure 20.** Values for methane delta carbon-13 and gas wetness for gas samples collected in the Aztec zone.

had a surface-casing pressure of 110 lb/in$^2$ in June 1990.

## SOURCES AND MIGRATION PATHWAYS OF NEAR-SURFACE GAS

This section describes sources of near-surface natural gas in the Animas River valley and the pathways and processes by which this gas migrates into aquifers and soil. Conclusions are based on information in previous sections of this report and on a conceptualization of local geology, mechanical aspects of features associated with gas production, and the dynamics of gas flow. A quantitative analysis of natural-gas sources is not feasible, given the uncertainties associated with some of the analyses discussed in the preceding section.

### Sources

Biogenic and thermogenic sources of gas exist in the near-surface environment of the study area. Biogenic gas is present locally in the Animas and Nacimiento Formations within several hundred feet of the land surface (and probably deeper). Biogenic gas was detected only in water samples from bedrock water wells and only in areas near the northern part of the study area and in a short reach of the Animas River valley from about 1 mi north of the Colorado-New Mexico State line to about 0.4 mi south of the State line. This gas formed by bacterial degradation of organic matter that was deposited in shales and mudstones and is trapped in contiguous sandstones. Water wells completed in alluvium are less likely to yield water containing biogenic gas than are wells completed in bedrock because of the coarse grain size of most alluvial deposits (in which conditions are unfavorable for deposition of organic material and trapping of methane) and the unconfined nature of alluvium (which allows oxidation of organic material). However, where bedrock shale is discontinuous because of stratigraphic pinchout or erosion and where bedrock water containing biogenic methane may discharge into alluvium, the likelihood of the alluvium containing biogenic gas increases.

Septic tanks are unlikely sources for natural-gas samples listed in table 4. Whiticar and others (1986, p. 699) list $\partial^{13}C_1$ values of -47.1‰ and -49.1‰ for sewage-sludge gas, which fall within the interval between -43.99‰ and -52.15‰ for all samples listed in table 4. Furthermore, septic-tank methane potentially affects methane concentrations in water in alluvium but has little potential to affect water in bedrock, in which the methane-detection frequency was 2.5 times that of water in alluvium (table 1). Septic-tank methane can neither invade gas-well casings nor provide adequate flux to account for the three soil seeps listed in table 4, all of which are located substantial distances downgradient from any houses and which probably leak from bedrock where buried river channels breach bedrock shale layers. No water wells completed in alluvium yielded a sufficient methane concentration for isotopic analysis. However, some of the methane detections for alluvial-water samples possibly resulted from migration of methane-laden water from septic tanks. The likelihood that sewage-derived methane accounts for a substantial fraction of methane detections in alluvial wells is discounted by 1) the spatial association of most methane-affected alluvial wells with methane-affected bedrock wells or near documented gas wells having gas leaks or uncemented annuli, and 2) clustering of most alluvial water wells not affected with methane in areas where housing densities are large (at and south of Cedar Hill, New Mexico) and where potential contamination with sewage products would be most likely to occur.

The discussion in the preceding section indicates that most gas in water, soil, external gas-well casings, and cathodic-protection wells probably is thermogenic gas from deep reservoirs. Thermogenic gas in the near-surface environment of the study area primarily originates from 1) conventional gas reservoirs, including the Dakota Sandstone, Mesaverde Group, Lewis Shale, and Pictured Cliffs Sandstone, and 2) coals in the Fruitland Formation. Less important sources include sandstones in the Fruitland Formation and the Kirtland Shale.

## Migration Pathways

The potential pathways along which thermogenic natural gas can migrate from deep reservoirs to the near-surface environment of the Animas River valley are rock pore spaces (by diffusion), natural fractures, and manmade conduits. Because vertical migration in the subsurface environment is not directly observable, an assessment of these three pathways is necessarily based on indirect, ancillary information. Consequently, none of these three pathways can be definitively discounted.

### Diffusion

Diffusion of thermogenic gas from source formations to the near-surface environment may have occurred in the study area. Diffusion is the movement of individual ions or gas molecules through water-saturated pore spaces in response to concentration gradients, in contrast to bulk, separate-phase movement of gas caused by buoyant forces or pressure gradients. Smith and others (1971) calculated that 140 million years would be required for methane to diffuse through a column of 1,740 m of clastic sediments. Leythaeuser and others (1982) calculated that one-half of the initial volume of methane in a gas field in Holland was dissipated through a 400-m-thick shale cap rock in 4.5 million years. Although diffusion can be an important gas-transfer process over geologic time, it is an extremely slow process that, within human life spans, contributes insignificant quantities of natural gas to the near-surface environment. Diffusion-transported gas either has not reached the near-surface environment of the study area from deep, gas-yielding formations or has not substantially accumulated in the near-surface environment. This conclusion is strongly supported by the fact that about 43 percent of bedrock sites had measured dissolved-methane concentrations less than 0.005 mg/L. Because diffusion occurs ubiquitously over gas deposits (which underlie the entire study area), if substantial quantities of gas had diffused intact to the near-surface environment and accumulated there, then greater background concentrations of dissolved gas would be measured. One possible explanation for the low background concentrations of methane is sulfate-reducing oxidation. Kelly and others (1985) demonstrated the ability of dissolved sulfate to oxidize methane. Cunningham (1988, p. 309) attributed extremely small concentrations of methane, ethane, and propane in soil gas overlying Cretaceous gas-yielding formations on the Four-Corners Platform (fig. 2) to possible near-surface biological utilization.

### Natural Fractures

To test the spatial relation between rock fractures and dissolved-methane data for the study area, fracture densities (Steven T. Finch, written commun., 1992) were correlated with fractions of the alluvial, bedrock, and total wells that had measurable concentrations of dissolved methane as reported in Chafin and others (1993). Wells were grouped by location in six subareas used by Steven Finch and John Shomaker (Steven T. Finch, written commun.,1992) (fig. 21). The Johnson water well (well 73 on pl. 1) was excluded because of the biogenic source of the dis-

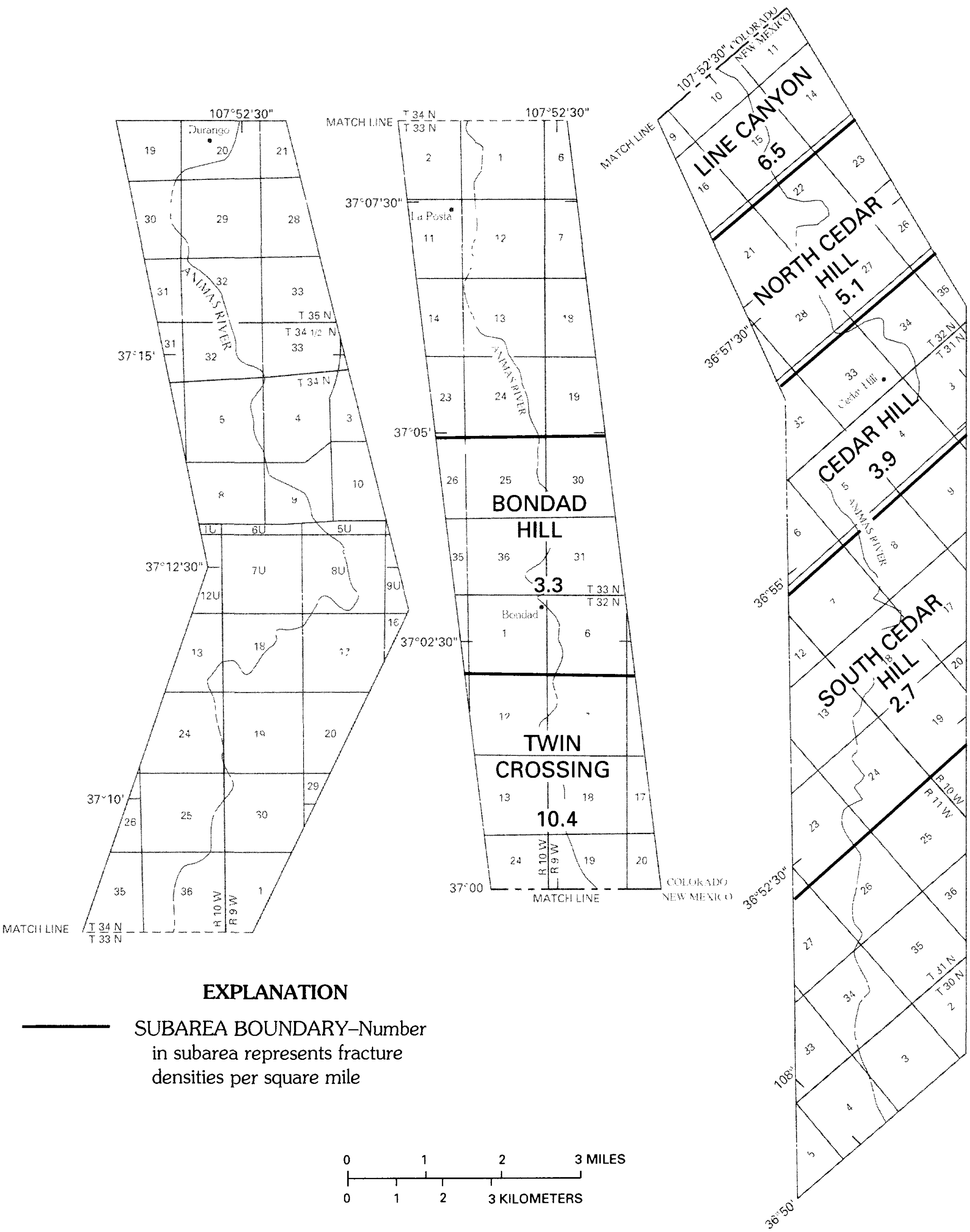



**Figure 21.** Subareas and corresponding fracture densities used for correlations between the fraction of methane-affected water wells and fracture density. Fracture densities are expressed in number per square mile.

solved gas, but the Kinslow water well (well 70 on pl. 1) was included because the $\partial^{13}C_1$ value indicates that some of the dissolved gas might have been thermogenic. Fracture densities and number of wells for the six subareas are listed in part A of table 5. Correlations were done for fractions of wells because of the variable number of wells between subareas. Correlations were done by ranks of variable values to avoid the necessity of assuming normal data distributions.

The results of these correlations (part B of table 5) do not indicate that fractures are substantial migration pathways between deep, gas-bearing formations and the near-surface environment. The fractions of alluvial and bedrock wells, as well as the fraction of all wells that contained detectable amounts of methane, all had negative correlations with fracture densities. Correlation coefficients (Spearman's rho, $R_s$) ranged from -0.086 to -0.580. Positive, not negative, correlations possibly would indicate deep fracture pathways. Although these correlations do not demonstrate a relation between dissolved-methane detections and the presence or density of fractures, they cannot disprove the possibility of local upward migration of methane along fractures.

Chemical and geological evidence suggests that substantial quantities of natural gas are not migrating from deep gas-bearing formations along natural fractures (joints and faults) into the shallow subsurface environment beneath the study area. Comparisons between soil-gas-methane concentrations measured adjacent to 352 gas-well casings and 192 ground-water sites (used as background measurements) indicate that gas-well annuli are more important than fractures for upward migration of gas. If natural fractures were the important conduits for upward migration, greater soil-gas-methane concentrations probably would be measured at some of the ground-water sites located on or near major fracture zones. The relatively systematic vertical and north-south variation in produced-gas maturities for formations beneath the study area argues against substantial vertical migration of gas and for effective trapping near source rocks. Most $\partial^{13}C_1$ values for near-surface environmental samples indicate reasonably distinct signatures of production gas from individual gas-yielding formations beneath the study

**Table 5.** Data and results for correlations between dissolved-methane detection frequency and fracture density

[A, input data for correlations; B, results for rank correlations; fracture densities are expressed as number per square mile; --, no data]

**A**

| Subarea (fig. 21) | Fracture density[2] | Number of wells[1] Alluvial: With methane | Alluvial: Total | Alluvial: Fraction with methane | Bedrock: With methane | Bedrock: Total | Bedrock: Fraction with methane | Combined: With methane | Combined: Total | Combined: Fraction with methane |
|---|---|---|---|---|---|---|---|---|---|---|
| Bondad Hill | 3.3 | 4 | 7 | 0.571 | 13 | 18 | 0.722 | 17 | 25 | 0.680 |
| Twin Crossing | 10.4 | 0 | 2 | .000 | 4 | 7 | .571 | 4 | 9 | .444 |
| Line Canyon | 6.5 | 0 | 2 | .000 | 0 | 5 | .000 | 0 | 7 | .000 |
| North Cedar Hill | 5.1 | 1 | 4 | .250 | 5 | 5 | 1.00 | 6 | 9 | .667 |
| Cedar Hill | 3.9 | 12 | 49 | .245 | 5 | 5 | 1.00 | 17 | 54 | .315 |
| South Cedar Hill | 2.7 | 7 | 29 | .241 | 0 | 0 | -- | 7 | 29 | .241 |

**B**

| Test statistic | Values by well types: Alluvial | Bedrock | Combined |
|---|---|---|---|
| Correlation coefficient ($R_s$) | -0.580 | -0.564 | -0.086 |
| Significance (p) | .228 | .322 | .872 |

[1]Data from Chafin and others (1993)

[2]Data from Steven T. Finch and John W. Shomaker (Steven T. Finch, John W. Shomaker, Inc., written commun., 1992)

area; fractures penetrating two or more producing formations would be expected to generally transport gas with mixed signatures to the near-surface environment. Correlations between dissolved-methane detection frequency and fracture density did not support general effects of fractures on methane concentrations in water from alluvial, bedrock, or combined wells.

Overpressuring of the coals in the Fruitland Formation (Kaiser and others, 1991) is another factor that tends to discount the hypothesis of substantial natural-fracture drainage of production gas from deep formations. Overpressuring is indicated by pressure gradients that exceed 0.433 $(lb/in^2)/ft$, which is the pressure gradient along a static column of relatively fresh water. In the vicinity of the study area, coals in the Fruitland Formation are overpressured north of a line located a few miles south of Cedar Hill (Kaiser and others, 1991, p. 204). Rice and others (1989, p. 623) concluded that this overpressuring is residual, having persisted since active gas generation in mid-Tertiary times. Overpressuring of coals in the Fruitland Formation is inconsistent with fracture drainage of gas for two reasons. First, overpressured zones indicate that the coals in the Fruitland Formation have been well confined since the Oligocene Epoch, which does not allow for substantial fracture breaching. Second, hydraulic considerations indicate that underpressured or normally pressured gas from underlying producing formations cannot migrate up natural channels into and through the coals in the Fruitland Formation. This gas would undergo pressure equilibration with normal or subnormal formation pressure in the Pictured Cliffs Sandstone and would not be able to flow into the overlying, overpressured coals in the Fruitland Formation.

The presence of thick shale units (fig. 4), the relatively simple geologic evolution of the San Juan Basin (minor faulting and folding and little or no erosion interrupting the deposition of gas-source and gas-reservoir formations), and the existence of substantial thermogenic gas deposits in the Dakota Sandstone, sandstones in the Mesaverde Group, Pictured Cliffs Sandstone, and the Fruitland Formation tens of millions of years after the gas was generated suggest that these major shale units are relatively effective seals that generally prevent separate-phase vertical migration of natural gas. Grunau (1981) reported that most caprock seals for gas fields are shales and that optimum conditions for seal preservation occur in areas that had a comparatively simple geologic evolution. Schowalter (1979) states that marine clay shales generally are considered to be regional caprock seals because of their small pores, ductility, and regional continuity. Rice and Claypool (1981, p. 11) considered bentonite beds in marine deposits of late Cretaceous age of the northern Great Plains to be excellent seals for widespread gas accumulations.

Lorenz and others (1991, p. 1720) concluded that fractures commonly are limited to more brittle rocks and usually terminate at contacts with more ductile rocks. This conclusion is substantiated by the observation by Tremain and Whitehead (1990) that joints (fractures without movement across the break) in sandstones of Cretaceous and Tertiary age cropping out on the northwestern side of the San Juan Basin invariably terminate at sandstone boundaries. Furthermore, when present, fractures in shale are more sparse than those in sandstone, and thicker beds of a given lithology have more widely spaced fractures (Lorenz and others, 1991, p. 1720). Beckstrom and Boyer (1991, p. 376-377) studied fracture-tracer surveys in the vicinity of Cedar Hill and concluded that fractures induced to complete coal-bed-gas wells in the Fruitland Formation were contained below the Kirtland Shale in all cases, which prevented fracture communication between coals in the Fruitland Formation and near-surface ground water. Considering these factors, joint propagation through the thick shale sequences of the Mancos Shale, Lewis Shale, Kirtland Shale, and the Nacimiento Formation is not likely to have occurred, and a network of continuous, interconnected joints between deep gas reservoirs and near-surface aquifers probably has never formed. That is not to say that more brittle components of shale have not fractured. Tremain and Whitehead (1990, p. 74) describe fractured oil and gas reservoirs in the siltstone and calcareous shale interbedded with plastic shale of the Mancos Shale, believed to occur in areas of maximum bed curvature associated with folding. Several similar small-scale fracture reservoirs are present in the Lewis Shale in the northern San Juan Basin (Thomaidis, 1978, p. 43-44). One such example (previously described in the section "Geology of the Study Area") occurs at 32N-09W-06BBD in Bondad at a depth of about 4,100 ft near the base of the Lewis Shale and in the vicinity of a fault. Gas in fractured-shale reservoirs probably resulted from short-distance migration that occurred early in the gas-generation phase, as described by Leythaeuser and others (1982, p. 426-427).

Faults (fractures with offsets across the break) formed during the Laramide orogeny (latest Cretaceous through Eocene (?) Epochs), when the San Juan Basin was being formed. Offsets of about 40 ft in the Pictured Cliffs Sandstone beneath Cedar Hill (Ambrose and Ayers, 1991, p. 50) do not offset beds of the Nacimiento Formation of Paleocene age at the surface, indicating a pre-Eocene age for those faults. Faults at Bondad (previously described in the section "Geology of the Study Area"), which offset the Nacimiento and lower San Jose Formations, do not offset the terrace bench of the Animas River valley of latest Eocene (or earliest Oligocene) age. No offset of this terrace or older terraces in the vicinity of the study area by faulting has been observed. This relation indicates that those faults occurred sometime during late Eocene (or earliest Oligocene times) after deposition of the lower San Jose Formation and before the lower terrace was formed by the Animas River. Terraces crossing the Hogback Moncline a few miles south of Durango are not displaced by movement. These age relations indicate that faulting in the study area preceded the major period of gas generation during the Oligocene Epoch, decreasing or eliminating the possibility for separate-phase, vertical migration of gas from deep reservoirs along faults. Downey (1984, p. 1756-1757) concluded that faults allow open passage for hydrocarbon migration along their fracture planes only under special conditions, the most significant one being shallow, near-surface faulting in a field of regional tensional stress. Thus, the substantial depths of gas reservoirs beneath the study area are unfavorable for upward migration of gas from them along fault planes. Furthermore, offsets of faults in the study area, including those in the Nacimiento Formation, are too small relative to thicknesses of major shale units beneath the study area to allow juxtaposition of interbedded sandstones and subsequent vertical migration of gas from great depths by networking through sandstones back and forth across faults. The ability of shales to trap hydrocarbons in sandstone reservoirs across faults is discussed by Smith (1966, p. 372) and Downey (1984, p. 1756). Although faults are unlikely to permit upward gas migration from deep reservoirs to the near-surface environment, locally, faults may permit migration between near-surface sandstones and alluvium (fig. 22).

Although fractures are not likely to provide effective migration pathways from deep, gas-producing formations to the near-surface environment, stress-relief fractures may permit upward migration of gas in the upper few hundred feet of bedrock beneath the Animas River valley. Several investigators (Ferguson, 1967; Borchers and Wyrick, 1981; Moebs and Sames, 1987; Moebs and Bauer, 1989; Molinda and others, 1991) describe vertical fractures and other unloading effects below the bottoms of valleys that have considerable topographic relief. Molinda and others (1991, p. 160) observed coal-mine failures to depths as great as 300 ft below the land surface because of these effects. Borchers and Wyrick (1981, p. 443) state that stress-relief fractures are near-surface phenomena that probably do not occur at depths greater than 100 or 200 ft. These fractures may permit gas to migrate upward between sandstones or sandstone and alluvium separated by relatively thin shales near the land surface (fig. 22).

### Manmade Conduits

Discussions in the section "Analysis of Isotopic and Molecular Composition of Gases from Water, Soil, Gas-Well Casings and Cathodic-Protection Wells" suggest that most occurrences of near-surface natural gas are related to conditions associated with gas wells. Given the previously described factors that are unfavorable for diffusion and natural-fracture migration pathways from deep gas reservoirs to the near-surface environment, it is reasonable to conclude that manmade migration conduits introduce most near-surface gas to the study area. For purposes of discussion, manmade migration pathways can be divided into 1) primary pathways, which transport gas from source formations to the subsurface environment, and 2) secondary pathways, which transport gas from primary pathways to the near-surface ground water and soil.

Primary migration pathways consist of leaking, conventional gas wells, and uncemented annuli of conventional gas wells through coals in the Fruitland Formation. Numerous examples of leaking, conventional gas wells in the study area are documented by COGCC and NMOCD records. Most such leaks are caused by either corroded or mechanically ruptured production casings or defective wellhead seals, which permit gas to leak from production casings into surface casings. Both types of leaks release gas into the uncemented annuli of gas wells, which are exposed to bedrock sandstones (fig. 23).

The second primary migration pathway for thermogenic gas in the study area is uncemented annuli of conventional gas wells through coals in the Fruitland Formation. Uncemented sandstones in the upper Fruitland Formation and Kirtland Shale can cause similar gas leakage into gas-well annuli, but these uncemented sandstones are less important pathways because they are not substantially charged with gas except locally. Coals in the Fruitland Formation are dewatered by pumping to promote desorption of gas from the coal matrix (Fassett, 1989, p. 133-134). Pumping induces a drawdown of the potentiometric surface in the coal around the well in the Fruitland Formation. Eventually, this lowered surface reaches offset conventional gas wells, and those wells without cemented annuli through the coals in the Fruitland Formation provide conduits for upward flow of desorbed gas (fig. 24). Beckstrom and Boyer (1991, p. 376) concluded that this process caused the accumulation of gas in the bradenheads of three conventional gas wells in the Cedar Hill area in 1989. Shuey (1990, p. 760) concluded that coals in the

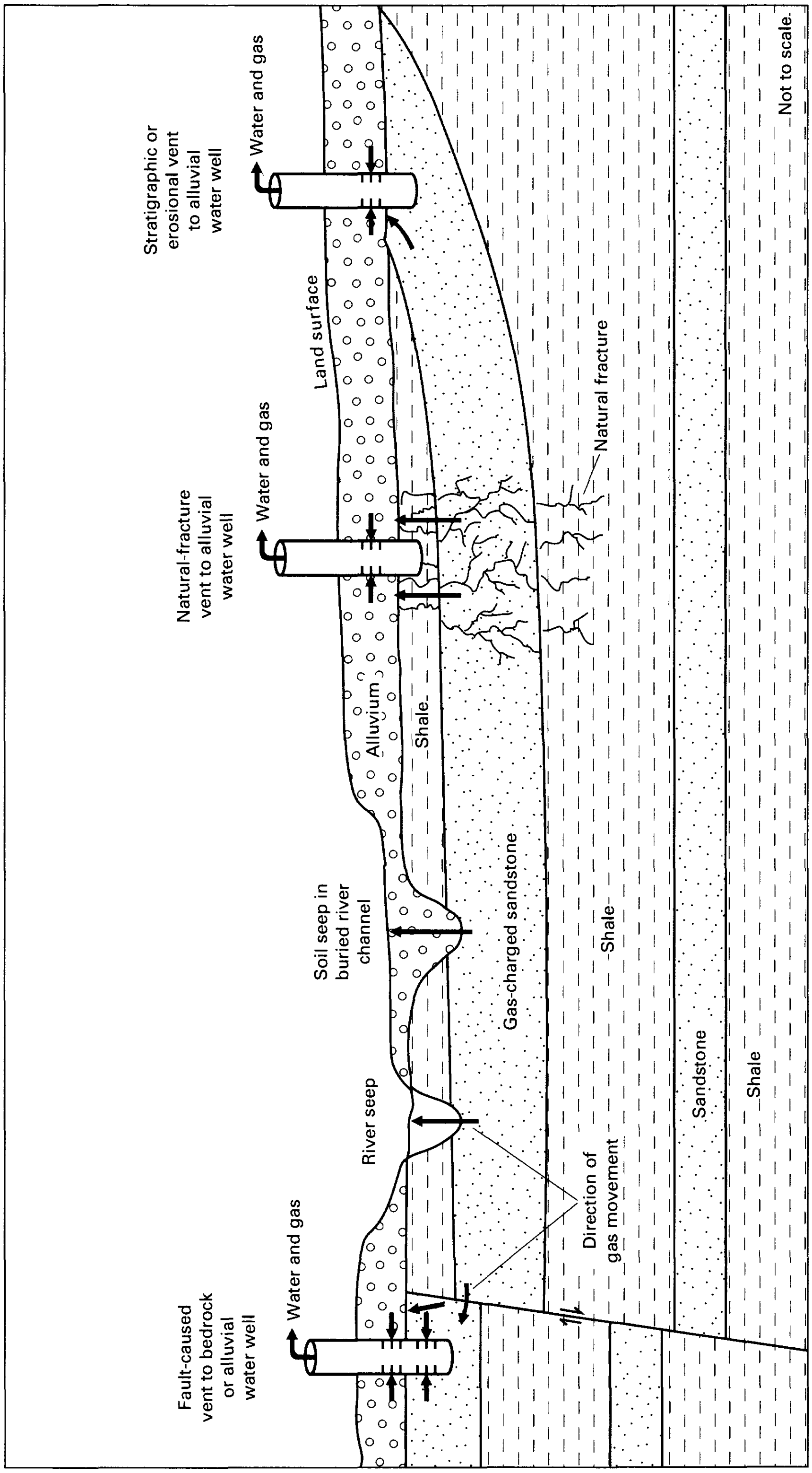



**Figure 22. Natural pathways of gas migration. Arrows show direction of gas movement.**

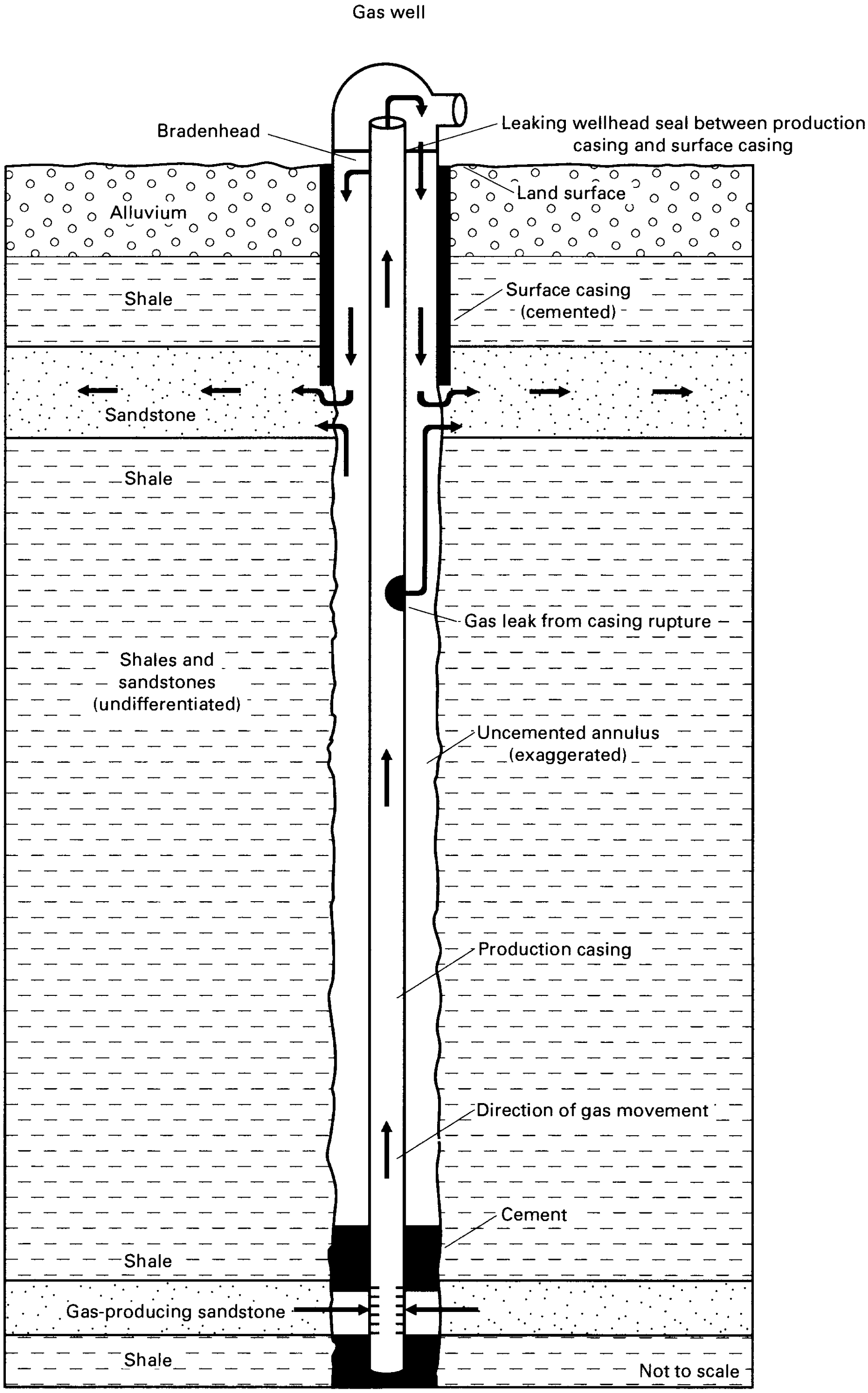



**Figure 23.** Types of leaks in conventional gas wells.

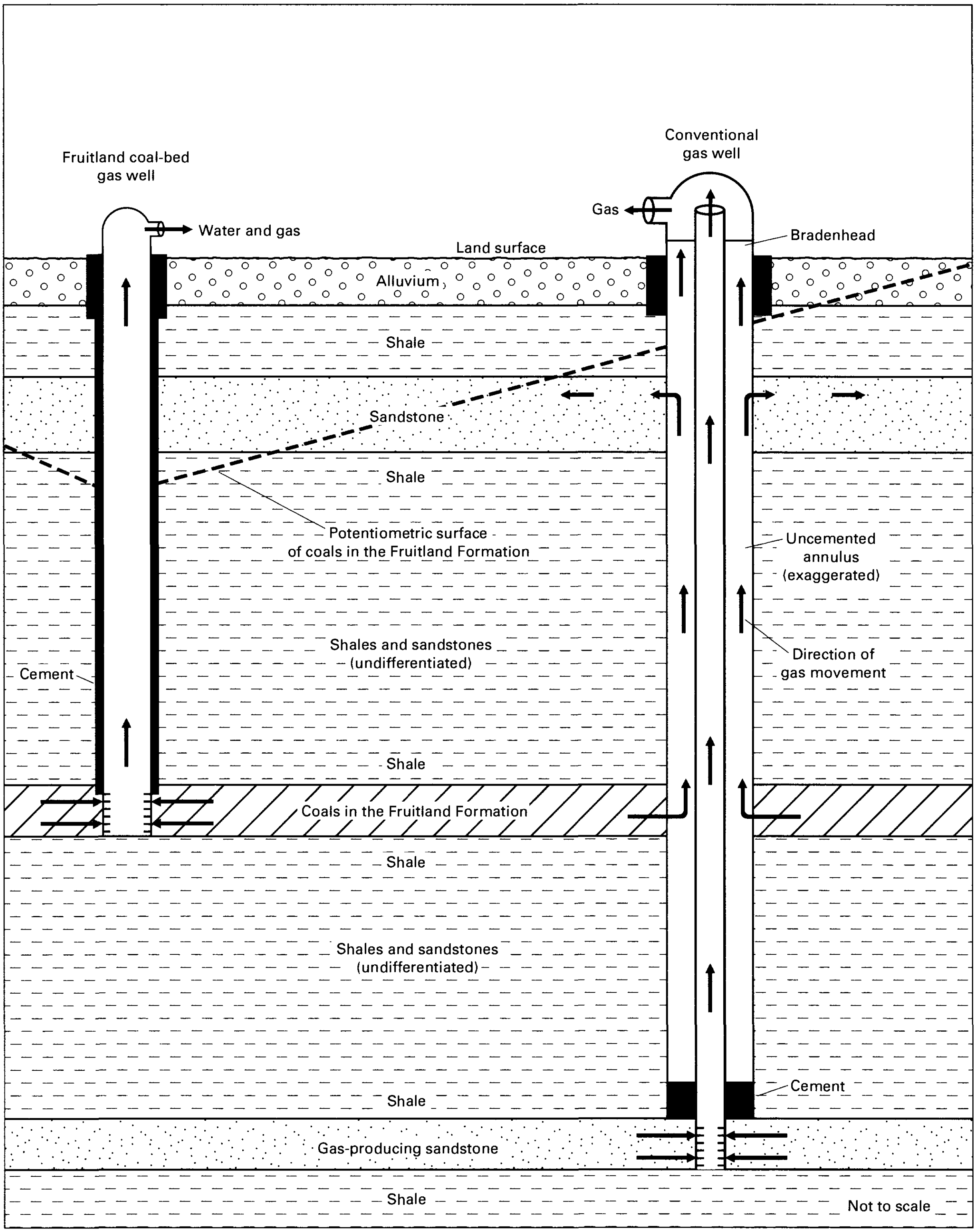



**Figure 24.** Gas leaking from depressurized coals in the Fruitland Formation into uncemented annulus of conventional gas well.

Fruitland Formation were the source of gas collected in 1989 from various gas-well annuli and cathodic-protection wells in the Cedar Hill area and in water samples at Bondad. He also (p. 760; fig. 4) invoked the above mechanism to account for the migration of the coal-bed gas from the Fruitland Formation.

Leakage from a primary pathway causes the growth of a column of gas in an uncemented annulus until rates for leakage and migration into the subsurface environment equalize or until the leak is repaired. Because of its low density compared to that of the surrounding water, this column of gas exerts a buoyant force upward against the confining layer at the top of the column (Schowalter, 1979, p. 724). According to Smith (1966, p. 364), gas pressure, $P_g$ (in pounds per square inch), along the column is equal to:

$$P_g = 0.433 \text{ (lb/in}^2\text{)/ft } [H\,(1.00 - \rho_g)], \qquad (3)$$

where

$H$ = height of gas column, in feet, and
$\rho_g$ = specific gravity of gas.

This equation assumes fresh water (density= 1.00 g/cm$^3$; a pressure gradient of 0.433 (lb/in$^2$)/ft), and neglects the small density gradient of gas over the column. The Ideal Gas Law can be used to estimate the specific gravity of methane. At 200 lb/in$^2$ and 15°C, methane density is about 0.009 g/cm$^3$. Use of this density as specific gravity in equation 3 allows the following approximation of pressure resulting from gas-column length:

$$P_g = 0.43 \text{ (lb/in}^2\text{)/ft } [H]. \qquad (4)$$

This approximation is reasonable for gas pressures as great as 1,000 lb/in$^2$ and all gas compositions in the near-surface environment of the study area. Equations 3 and 4 assume that the gas column protrudes little or no height above the water table; gas columns in annuli above deeper water tables (such as on mesas and hills adjacent to the Animas River valley) may exhibit substantially smaller bradenhead pressures for their gas-column lengths than estimated by equation 4.

Because gas pressure is about equal along the length of the gas column, gas has the greatest potential to enter sandstones near the top of the column and close to the land surface, where permeabilities may be greater because of near-surface fracturing, and where counter-pressure from the water column, $P_w$ (in pounds per square inch), is smallest according to the relation:

$$P_w = 0.433 \text{ (lb/in}^2\text{)/ft } [Z], \qquad (5)$$

where

$Z$ = depth, in feet, below water table or potentiometric surface.

Equation 5 describes the approximate minimum casing pressure required at given depths below the water table for a ruptured gas-well casing to leak gas into an annulus. For example, at a depth of 1,000 ft, a casing pressure that exceeds about 433 lb/in$^2$ would permit gas to leak from a ruptured casing. Lesser casing pressures would cause water to flow into the casing and eliminate gas flow from the producing formation unless formation-pressure recovery caused gas pressures to increase to a level exceeding the local water pressure. This pressure-depth relation suggests that higher pressures associated with (1) shut-in (nonflowing) gas wells, (2) gas wells producing from deeper formations with greater gas pressures than those in shallower formations, and (3) newer gas wells with less depleted producing-formation pressures would have relatively greater capacities to leak gas at greater depths than would older gas wells. Casing pressures of leaking gas wells limit the growth of gas columns in annuli to maximum lengths, according to equation 4. Actual lengths may be shorter because of continuous leakage into sandstones (crossflow).

Secondary migration pathways are required to transport gas from primary migration pathways to the near-surface environment because of the presence of abundant, relatively impermeable shales in the subsurface. Shales, except where thin and fractured, cannot transmit substantial quantities of gas (except over geologic time). Secondary migration pathways largely consist of gas-well annuli, cathodic-protection wells, seismic-test holes, and bedrock water wells. Gas-well annuli are the predominant secondary migration pathways because leaks from gas-well casings and from uncemented, gas-yielding coals and sandstones occur within them and because of their great number and depth in the study area; they allow the most direct vertical transport of gas from gas-well leaks and uncemented source formations to the near-surface environment.

Because surface casings of most conventional gas wells in the study area extend to depths of 150 to 300 ft, other secondary migration pathways besides gas-well annuli are required to transport gas up to the levels of all but a few bedrock water wells in the study area. Sandstones in bedrock formations seldom are thicker than 20 ft and do not adequately connect the annuli at the bottom of surface casings to much higher horizons. Cathodic-protection wells can act as vertical conduits between deeper, gas-charged sandstones and near-surface sandstones and alluvium used for water supplies. These wells are emplaced at most gas-well sites but can serve multiple gas wells. Cathodic-protection wells, usually at least 250 ft deep, are backfilled with coke, and, in river alluvium, typically have uncemented surface casings set to depths of 20 to 60 ft (Beckstrom and Boyer, 1991, p. 375). Seismic-test holes are drilled to depths of several hundred feet, are uncased, and usually are backfilled with excavated earth materials. These holes permit upward transport of gas in the same way as do cathodic-protection wells but are not as numerous in the study area and generally are further from gas wells. Bedrock water wells generally do not permit upward transport of substantial amounts of gas into aquifers because they generally are cased only through alluvium, which prevents the buildup of substantial gas pressure in an annular space. Also, because bedrock water wells are not backfilled as are cathodic-protection wells and seismic-test holes, gas released into their bores bubbles upward and usually escapes to the atmosphere at the top of the casing. Well bores (unless sealed) cannot sustain gas pressures sufficient to force substantial quantities of gas to flow into upper layers of sandstones or alluvium. However, bedrock wells may permit sufficient upward gas migration to affect dissolved-methane concentrations in downgradient, nearby shallower water wells.

Migration of gas along secondary migration pathways is illustrated in figure 25. Gas can migrate into sandstones (crossflow) below the fully cemented interval between the land surface and the casing leak (provided the gas pressure is sufficient at that depth). This migration occurs below the intermediate string of a three-stage well (when the intermediate casing is effectively cemented to surface) and below the surface casing of a two-stage well (or a three-stage well when the intermediate casing is not cemented to the surface). Crossflow also can occur above these levels if channels in the cement permit upward migration of gas. Kirksey and Warembourg (1979, p. 275) list some of the factors causing ineffective cement seals:

- Cement contamination by mud.
- Loss of fluid from cement slurry.
- Gas cutting of cement before set.
- Lost circulation before or during cementing.
- Breakdown of zones after cementing (fallback).
- Salt and coal sections.

Increased soil-gas-methane concentrations adjacent to the casings of numerous gas wells in the study area (Chafin and others, 1993) indicate that the cement around many surface casings does not effectively prevent upward migration of gas from the annuli of those wells.

Gas migrates horizontally through sandstones in response to pressure gradients. Origin pressures are determined by gas-column lengths, as described by equation 4, or casing-leak pressures when they are adjacent to sandstones with smaller hydrostatic pressures. Because of the buoyant force of the gas in the sandstone pores, the gas will flow upward until it reaches the base of the overlying shale. Therefore, gas generally migrates along the upper part of sandstone layers unless gas-flow rates are sufficient to locally fill the entire thickness of the sandstone. As illustrated in figure 25, where the gas contacts a relatively open, vertical conduit, buoyant forces will cause it to flow upward and possibly establish another column that can establish crossflow into other sandstones nearer the land surface.

The preceding discussion of migration pathways is consistent with the more frequent detections and generally greater concentrations of methane in water from wells completed in bedrock compared to water from wells completed in alluvium. Gas originates in bedrock and will reach bedrock wells before alluvial wells during upward migration. Bedrock is more confined than alluvium and will trap gas more effectively. Ground-water velocities generally are faster in alluvium than in bedrock and can effectively dilute and disperse gas leaking from bedrock. Alluvium becomes charged with gas at and downgradient from natural and manmade escape vents that penetrate bedrock shale layers where gas is trapped.

## SUMMARY

In July 1990, the U.S. Geological Survey began a study of near-surface ground water in the Animas River valley in the San Juan Basin between Durango, Colorado, and Aztec, New Mexico, to identify the sources and migration pathways of natural gas.

Most measured methane concentrations in ground water of the study area during August-November 1990 were less than the analytical reporting limit of 0.005 mg/L. Samples collected from 70 out of 205 sites (34 percent) had concentrations exceeding the reporting limit. The maximum concentration was 39 mg/L, and the mean concentration of methane for all 205 samples was 1.3 mg/L. The concentrations of dissolved methane in water samples collected from wells completed in bedrock generally were greater than concentrations in samples from wells completed in alluvium. Mean concentrations were 0.14 mg/L for all wells in alluvium and 3.6 mg/L for all wells in bedrock.

Correlations were made between dissolved-methane concentrations and specific conductance, pH, temperature, and alkalinity; between dissolved-methane concentrations and concentrations of dis-

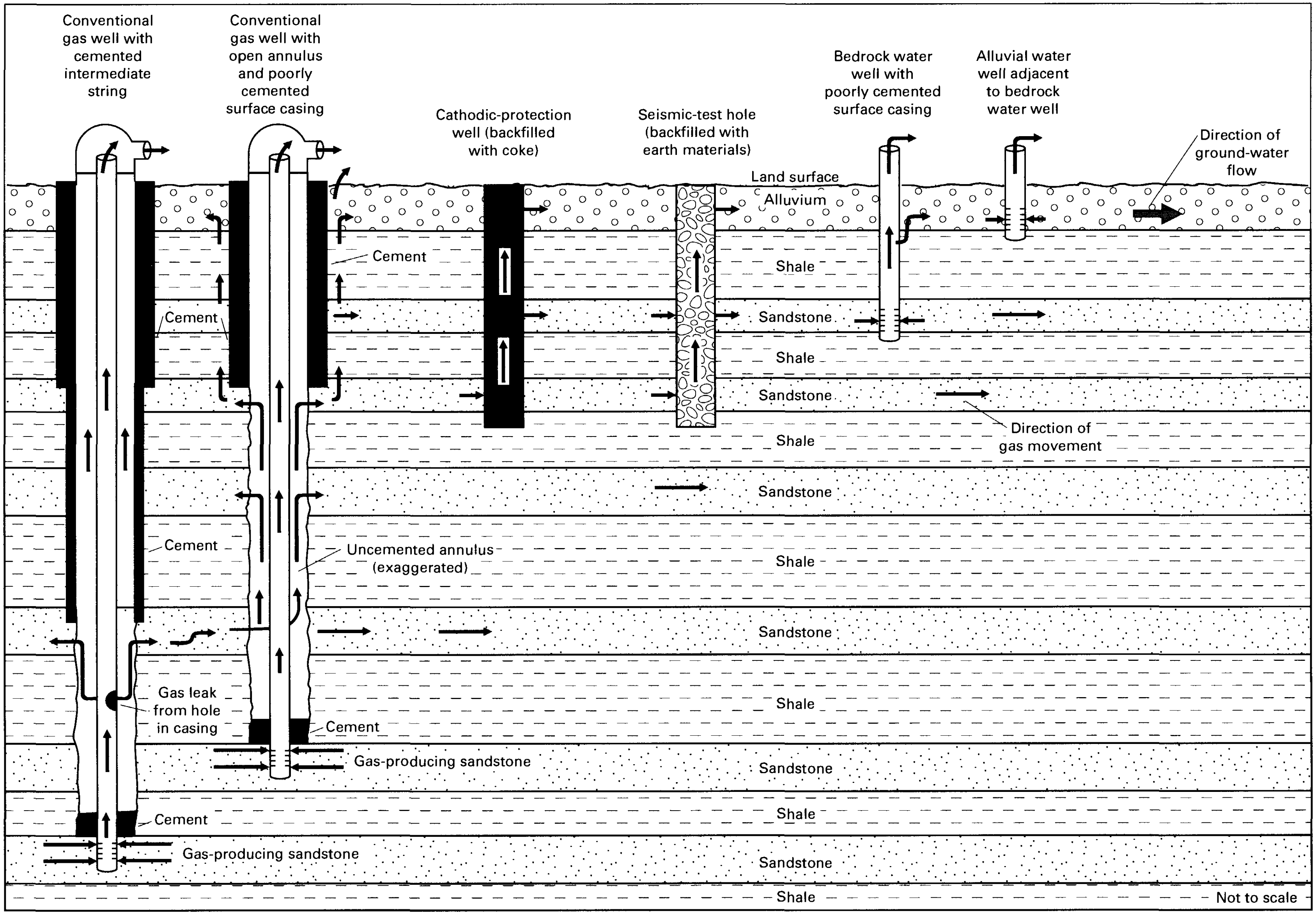



**Figure 25.** Manmade pathways of gas migration.

solved solids, major ions, bromide, silica, iron, and manganese; and between dissolved-methane concentrations and equilibrium $CO_2$ pressure. No substantial correlation resulted for water-quality data for alluvial, bedrock, or combined sites, probably because of the complex variety of water-quality compositions in alluvial and bedrock aquifers. Dissolved methane was detected in ground water at only 41 of 164 (25 percent) sites at which hydrogen sulfide ($H_2S$) was not present (the mean methane concentration was about 0.55 mg/L), and at 29 of 41 (about 71 percent) of sites at which $H_2S$ was present (the mean methane concentration was 4.1 mg/L).

Soil-gas-methane concentrations at only 5 of 192 ground-water sites were greater than the reporting limit of 0.005 mg/$L_g$, even at sites where large dissolved-methane concentrations in the ground water itself were measured. The lack of a relation between ground-water-methane concentrations and nearby soil-gas-methane concentrations indicates that soil-gas surveys are not definitive in delineating areas in this study area where ground water is charged with gas. However, soil-gas measurements were used to document four gas seeps in open fields.

Soil-gas-methane concentrations were measured adjacent to 352 gas-well casings. The analytical reporting limit of 0.005 mg/$L_g$ was equaled or exceeded by 40 percent of measurements. Concentrations of at least 100 mg/$L_g$ were measured in 25 samples (7 percent) up to a maximum concentration of 1,200 mg/$L_g$.

Potential sources of dissolved and soil gases collected as part of this study were determined by comparing their isotopic ($\partial^{13}C_1$) and molecular compositions to those compositions for produced formation gases and biogenic gases and by incorporating pertinent information about gas-well construction or leaks. Additional analyses of gas samples collected by COGCC and NMOCD in 1989 and 1990 from surface and intermediate casings of gas wells, from cathodic-protection wells, and from gas-yielding formations also were used.

Biogenic and thermogenic gas is present in the near-surface environment of the study area. Biogenic gas, which is present locally in the near-surface Animas and Nacimiento Formations, was formed by bacterial degradation of organic matter that was deposited in shales and mudstones and is trapped in contiguous sandstones. Most near-surface gas probably is thermogenic gas from deep reservoirs. This gas primarily originates from 1) conventional gas reservoirs, including the Dakota Sandstone, Mesaverde Group, Lewis Shale, and Pictured Cliffs Sandstone; and 2) coals in the Fruitland Formation. Less important sources of thermogenic gas include sandstones in the upper Fruitland Formation and the Kirtland Shale.

The potential pathways along which thermogenic natural gas can migrate from deep reservoirs to the near-surface environment are rock pore spaces (by diffusion), natural fractures, and manmade conduits. Although diffusion of natural gas from producing formations to the near-surface environment may have occurred, and diffusion is an important gas-transfer process over geologic time, it is an extremely slow process that, within human lifespans, contributes insignificant quantities of natural gas to the near-surface environment. Any diffusion-transported gas has not accumulated in the near-surface environment of the study area (assuming it has reached there), possibly because of anoxic (sulfate-reducing) oxidation in near-surface bedrock.

Dissolved-methane concentrations measured for this study were correlated with fracture densities mapped by other investigators. The fractions of alluvial and bedrock wells, as well as the fractions of all wells that contained detectable amounts of methane, all had negative correlations with fracture densities. These results do not indicate that fractures are substantial migration pathways between deep, gas-bearing formations and the near-surface environment.

Chemical and geological evidence suggests that substantial quantities of natural gas are not migrating from deep gas-bearing formations along natural fractures into the shallow subsurface environment beneath the study area. Comparisons between soil-gas-methane concentrations measured adjacent to 352 gas-well casings and 192 ground-water sites used as background measurements indicate that gas-well annuli are more important than natural fractures for upward migration of gas. The systematic variation in produced-gas maturities for formations beneath the study area argues against substantial vertical migration of gas through fractures and for effective trapping near source rocks. Residual overpressuring of coals in the Fruitland Formation beneath most of the study area, the presence of major shale units, the relatively simple geologic evolution of the San Juan Basin, and the existence of substantial thermogenic gas deposits in the Dakota Sandstone, sandstones of the Mesaverde Group, Pictured Cliffs Sandstone, and the Fruitland Formation tens of millions of years after gas generation indicate that these major shale units are relatively effective seals that prevent separate-phase, vertical migration of natural gas along fractures. The lack of fault offsets of the terrace bench of the Animas River valley of late Eocene (or earliest Oligocene age) indicates that faulting in the study area predates the major period of gas generation during the Oligocene, decreasing or eliminating the possibility for separate-phase, vertical migration of gas from deep reservoirs along faults.

Manmade migration pathways probably introduce most near-surface gas to the study area. Primary migration pathways consist of 1) leaking, conventional gas wells and 2) uncemented annuli of conventional gas wells along coals in the Fruitland Formation. Uncemented annuli along sandstones in the upper Fruitland Formation and Kirtland Shale introduce less gas than coals in the Fruitland Formation because these sandstones are not substantially charged with gas, except locally. Secondary migration pathways consist of gas-well annuli, cathodic-protection wells, seismic-test holes, and bedrock water wells. Of these, gas-well annuli are the predominant secondary migration pathway because leaks from gas-well casings and from uncemented, gas-yielding coals and sandstones occur within them and because of their great number and depth.

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