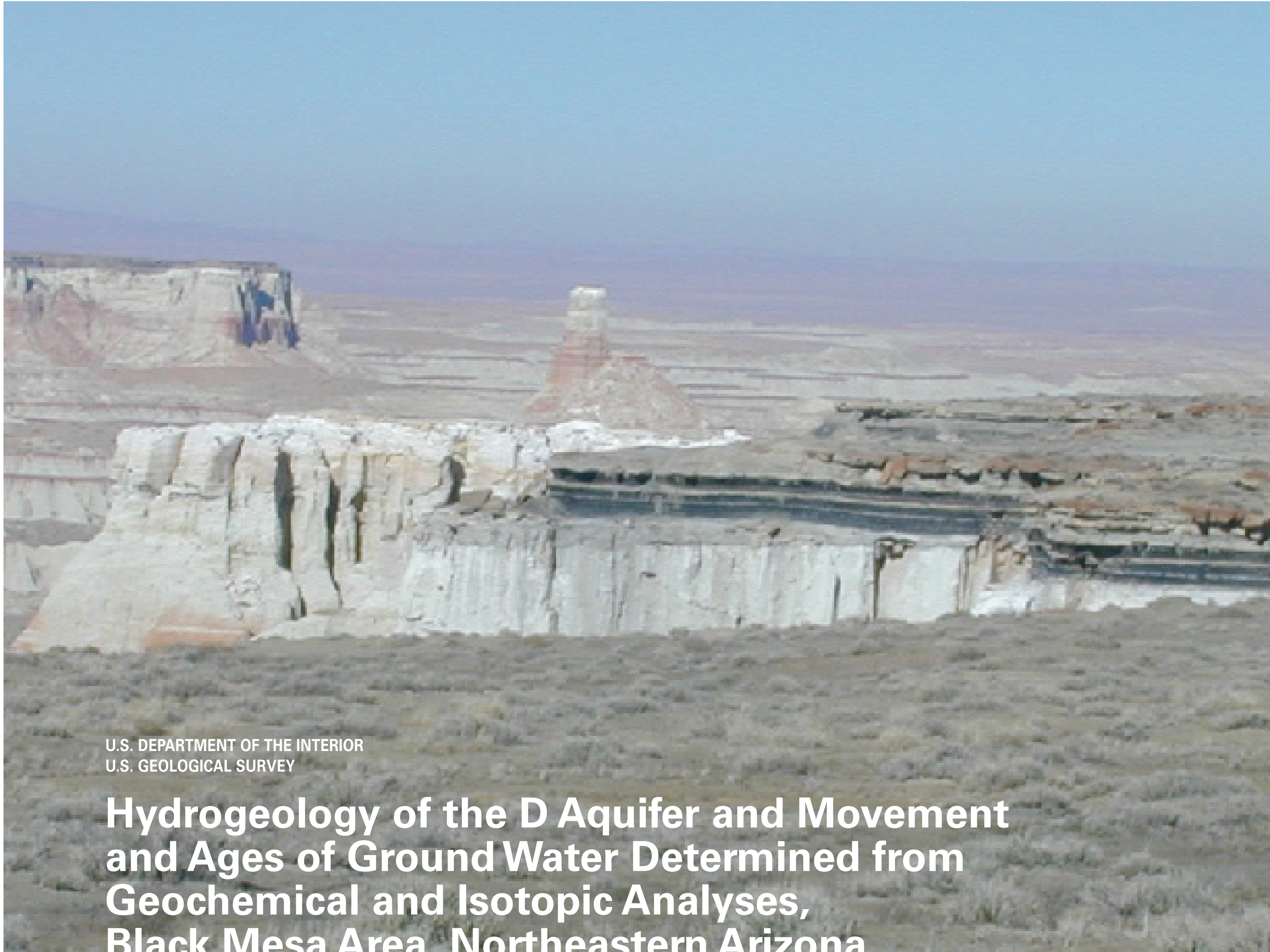

U.S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

# Hydrogeology of the D Aquifer and Movement and Ages of Ground Water Determined from Geochemical and Isotopic Analyses, Black Mesa Area, Northeastern Arizona

Water-Resources Investigations Report 03—4189 Version 1.1

*Prepared in cooperation with the BUREAU OF INDIAN AFFAIRS*

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U.S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

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*By* Margot Truini *and* Steve A. Longsworth

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Tucson, Arizona
2003

U.S. DEPARTMENT OF THE INTERIOR
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## CONVERSION FACTORS AND DATUMS

| Multiply | By | To obtain |
|---|---|---|
| inch (in) | 2.54 | centimeter |
| inch (in) | 25.4 | millimeter |
| foot (ft) | 0.3048 | meter |
| mile (mi) | 1.609 | kilometer |
| acre-foot (acre-ft) | 1,233 | cubic meter |
| acre-foot (acre-ft) | 0.001233 | cubic hectometer |
| acre-foot per year (acre-ft/yr) | 1,233 | cubic meter per year |
| acre-foot per year (acre-ft/yr) | 0.001233 | cubic hectometer per year |
| picocurie per liter (pCi/L) | 0.037 | becquerel per liter |

Temperature in degrees Celsius (° C) can be converted to degrees Fahrenheit (° F) as follows:

$$°F=(1.8°C)+32$$

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29)—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; horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27). **Altitude**, as used in this report, refers to distance above or below NGVD 29.

## ABBREVIATED WATER-QUALITY UNITS

Chemical concentration and water temperature are given only in metric units. Chemical concentration in water is given in milligrams per liter (mg/L) or micrograms per liter (μg/L). Milligrams per liter is a unit expressing the solute mass (milligrams) per unit volume (liter) of water. One thousand micrograms per liter is equivalent to 1 milligram per liter. For concentrations lower than 7,000 milligrams per liter, the numerical value is about the same as for concentrations in parts per million. Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25° C). Radioisotope activity is expressed in picocuries per liter (pCi/L), the amount of radioactive decay producing 2.2 disintegrations per minute in a unit volume (liter) of water. Stable-isotope ratios are reported relative to internationally agreed upon standards. Deviations from standards are expressed in per mil (‰) using the delta (δ) notation. The delta symbol in this report is followed by the chemical symbol for the heavier isotope measured during isotopic analysis. Isotopic values are described as lighter or heavier in relation to each other. Lighter isotopic values are smaller or more negative per mil values, and heavier isotopic values are larger or more positive per mil values.

## ABBREVIATED ELEMENT NAMES

| | |
|---|---|
| Al | Aluminum |
| B | Boron |
| C | Carbon |
| Ca | Calcium |
| Fe | Iron |
| H | Hydrogen |
| K | Potassium |
| Li | Lithium |
| Mg | Magnesium |
| Mn | Manganese |
| N | Nitrogen |
| Na | Sodium |
| O | Oxygen |
| S | Sulfur |
| Sr | Strontium |
| Si | Silicon |
| Ti | Titanium |
| Zr | Zirconium |

# Hydrogeology of the D Aquifer and Movement and Ages of Ground Water Determined from Geochemical and Isotopic Analyses, Black Mesa Area, Northeastern Arizona

*By* Margot Truini *and* Steve A. Longsworth

## Abstract

The Navajo Nation and the Hopi Tribe in the Black Mesa area depend on ground water from sandstones of the N aquifer for domestic, agricultural, municipal, and industrial needs. They are concerned that pumping of water from the N aquifer will induce leakage from the overlying D aquifer, resulting in the degradation of water quality in the N aquifer. Water samples from the D aquifer contained higher concentrations of dissolved solids than samples from the N aquifer; however, ground waters in the D and N aquifers evolve similarly along their respective flow paths.

The ground-water composition in the D aquifer results from interaction with limestone and sandstone sediments. The ground water evolves from a calcium magnesium bicarbonate type in the recharge area to a sodium bicarbonate type in downgradient areas. $^{34}S$ data indicate sulfate reduction occurs when ground water comes in contact with lignite seams in the Dakota Sandstone. Adjusted $^{14}C$ ages for ground water in the D aquifer range from 4,000 to 33,000 years. $\delta^{18}O$ and $\delta^{2}H$ data indicate that most of the recharge occurred when the climate was cooler and more humid than at present. $^{3}H$ data indicate that localized recharge has occurred in some areas in recent time.

Leakage between the D and N aquifers has been occurring for thousands of years. The area of highest leakage occurs in the southern areas of Black Mesa, where the N aquifer is thin, the predevelopment hydraulic gradient is small, and the vertical head differences between the D and N aquifers are small. Induced leakage from ground-water development in the last several decades could take centuries to detect geochemically because of the increased vertical difference between the potentiometric surfaces of the D and N aquifers, and possibly because of increases in the hydraulic gradient in the N aquifer that would increase flow rates, causing dilution.

$^{87}Sr/^{86}Sr$ data are consistent with the leakage of ground water from the D aquifer into the N aquifer in the southern part of Black Mesa. $^{87}Sr/^{86}Sr$ values for the N and D aquifers are similar in this area; statistical means are -2.74 ‰ and -2.49 ‰, respectively. N aquifer $^{87}Sr/^{86}Sr$ values are more radiogenic than D aquifer values in the northern part of Black Mesa; statistical means are -0.14 ‰ and -2.49 ‰, respectively.

# INTRODUCTION

The Navajo Nation and the Hopi Tribe are concerned that ground-water leakage to the N aquifer from the overlying D aquifer could degrade the quality of water in the N aquifer. Ground water from the N aquifer in the Black Mesa area, northeastern Arizona, is used by the Navajo Nation and the Hopi Tribe for household, agricultural, municipal, and industrial purposes, and by Peabody Western Coal Company (PWCC) for its slurry line that transports coal from a mine in the area to the Mohave Generating Station in Laughlin, Nevada, 273 mi away. Water from the D aquifer is withdrawn only by windmills for livestock watering and by a few municipal wells for local household uses; it typically is high in dissolved solids and unsuitable for human consumption. In 1993 GeoTrans Incorporated (1993) reported that chemical similarities between the two aquifers in some areas indicate leakage of ground water from the D aquifer to the N aquifer.

Lopes and Hoffmann (1997) classified wells in the N aquifer into two groups on the basis of the likelihood that water chemistry in the N aquifer was affected by leakage from the D aquifer. Geographically, the group of wells apparently affected by leakage are in the southeastern part of Black Mesa where the N aquifer thins to extinction, the lateral flow velocity of water in the N aquifer was small before 1960, the D aquifer overlies the N aquifer, and hydraulic head in the D aquifer generally exceeds head in the N aquifer. Water from wells in this group had higher concentrations of boron and chloride than other N-aquifer wells, and the concentrations were similar to those in the D aquifer. Dissolved-oxygen concentrations within the group were lower than in other N-aquifer wells. These factors suggest that leakage from the D aquifer to the N aquifer was a feature of the regional flow system long before significant ground-water pumpage began.

Owing to the complex lithology of the D aquifer, however, it is difficult to determine where increased leakage to and degradation of the N aquifer is most likely to occur. The need for additional water-chemistry data from the D aquifer to better estimate leakage to the N aquifer was stated by Lopes and Hoffmann (1997). That study prompted this cooperative study by the Bureau of Indian Affairs (BIA) and the U.S. Geological Survey (USGS) during 1997–2001. The study area covers about 11,000 $mi^2$ on Black Mesa and includes the Navajo and Hopi Indian Reservations (**fig. 1**).

## Purpose and Scope

The purpose of this report is to improve the understanding of leakage between the D and N aquifers that may have existed before substantial ground-water withdrawls from the N aquifer and the resulting changes from that development. The focus of this report is the D aquifer. This report describes the hydrogeology of the D aquifer and relations between the D aquifer and N aquifer on the basis of geochemical and isotopic data analyses. Geochemical and isotopic data were used to compare flow-path evolution in the D and N aquifers, estimate ground-water ages in the D aquifer, describe recharge to the D aquifer, and examine ground-water leakage from the D to the N aquifer.

## Acknowledgments

The Navajo Department of Water Resource Management; the Navajo Tribal Utility Authority; the Bureau of Indian Affairs, Navajo Region; and members of the Piñon, Black Mesa, Forest Lake, Blue Gap, Rough Rock, and Rocky Ridge Chapter Houses provided access to the sites and valuable information about the construction and history of the wells, and helped in the collection of hydrogeologic data. The Hopi Tribe provided assistance and helped in obtaining water-chemistry and water-level data from wells. PWCC assisted in the collection of ground-water data from its wells.

# STUDY METHODS

Water and rock samples were collected and analyzed to determine the directions of ground-water movement, describe ground-water chemistry evolution along flow paths, determine ground-water ages in the D aquifer, and better describe the hydrogeologic relation between the D and N aquifers. Drillers' and geologists' logs were used to differentiate hydrogeologic units at sampled wells. Chemical and water-level data from previous studies were used in the analyses, and water levels were measured at wells sampled during this study when possible. Inverse geochemical modeling and graphical and statistical methods were used to analyze the chemical data.

## Sample Sites

Well and spring sites and rock-sample locations were selected for ground-water and solid-phase sample collection and chemical analyses. Wells completed in the D and N aquifers were selected for sampling on the basis of depth and perforated interval, location, accessibility, and aquifer-unit association (**fig. 1**). For most of the D aquifer wells, the depth from which the sample was collected included large perforated intervals and varied lithology. Water samples were collected from 11 windmills and 2 municipal wells completed in the D aquifer and from 15 wells completed in the N aquifer. Additional water samples were collected from 3 municipal wells that were completed in the N aquifer and later received some water from the D aquifer through breaks in the casings.

Three springs that discharge from units of the D aquifer were selected because they were accessible and their discharges were amenable to sampling. Many springs identified from the USGS database as D aquifer discharge points either turned out to be dry, had been developed and did not allow access to the source, or no longer existed. Two of the springs were undeveloped and one was developed with a collection chamber. Water samples were collected from the undeveloped springs by allowing the water to drip into the bottles. Water samples were collected from the developed spring through a pipe connected to the collection chamber.

Rock samples were collected from two road cuts along the northeast side of Black Mesa. The first road cut is along a dirt road near Rough Rock where rocks of the Morrison Formation, Dakota Sandstone, Mancos Shale, and Mesa Verde Group are exposed. The second road cut is along State Route 59 between Rough Rock and Chilchinbito where rocks of the Navajo Sandstone, Carmel Formation, Entrada Sandstone, Morrison Formation, and Dakota Sandstone are exposed. Unweathered samples were obtained by digging into the faces of the rock units.

## Collection and Analysis of Water and Rock Samples

Water samples from wells and springs were analyzed for major ions, minor ions, and selected stable and radioactive isotopes. Rock samples were analyzed for $^{18}O/^{16}O$ and $^{34}S/^{32}S$ from sulfate, $^{13}C/^{12}C$, and $^{87}Sr/^{86}Sr$ (**table 1**). Ground water from D aquifer wells was analyzed for major and minor ions and stable and radioactive isotopes. Ground water from N aquifer wells was analyzed for stable isotopes, and ground water from selected N aquifer wells was analyzed for radioactive isotopes. At Owl Spring and Upper Badger Spring, samples were collected only for $^{18}O/^{16}O$ and tritium ($^{3}H$) analyses because low discharges precluded collection of sample volumes sufficient for additional analyses. For Rough Rock Spring, only analyses for $^{87}Sr/^{86}Sr$, $^{18}O/^{16}O$ and $^{34}S/^{32}S$ from sulfate, $^{11}B/^{10}B$, $^{18}O/^{16}O$, $^{13}C/^{12}C$, $^{14}C$, and several major ions are available because some samples were damaged during processing.

Well-, spring-, and rock-sample data were used to aid in defining a variety of processes. Major- and minor-ion data were used to describe the chemical composition of ground water in the D aquifer and understand ground-water flow-path evolution. Stable-isotope ratios ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) were used to investigate sources of ground-water recharge. Stable-isotope ratios ($^{34}S/^{32}S$ and $^{18}O/^{16}O$) from sulfate and boron-isotope ratios ($^{11}B/^{10}B$) were used to describe flow-path processes and identify potential isotopic signatures unique to the D and N aquifers. $^{13}C/^{12}C$, $^{14}C$, and $^{3}H$ data were used to adjust ground-water ages.

To ensure that water samples were representative of water in the aquifer, specific conductance, pH, dissolved oxygen, and water temperature were monitored in the field until they stabilized in the pumped discharge. Water samples collected for analyses of major and minor ions, $^{13}C/^{12}C$, $^{14}C$, and $^{87}Sr/^{86}Sr$ were filtered using 0.45-micrometer filters. Samples for metals, metalloids, most cations, and $^{87}Sr/^{86}Sr$ were preserved in the field by using nitric acid ($HNO_3$) to lower the pH to below 2.

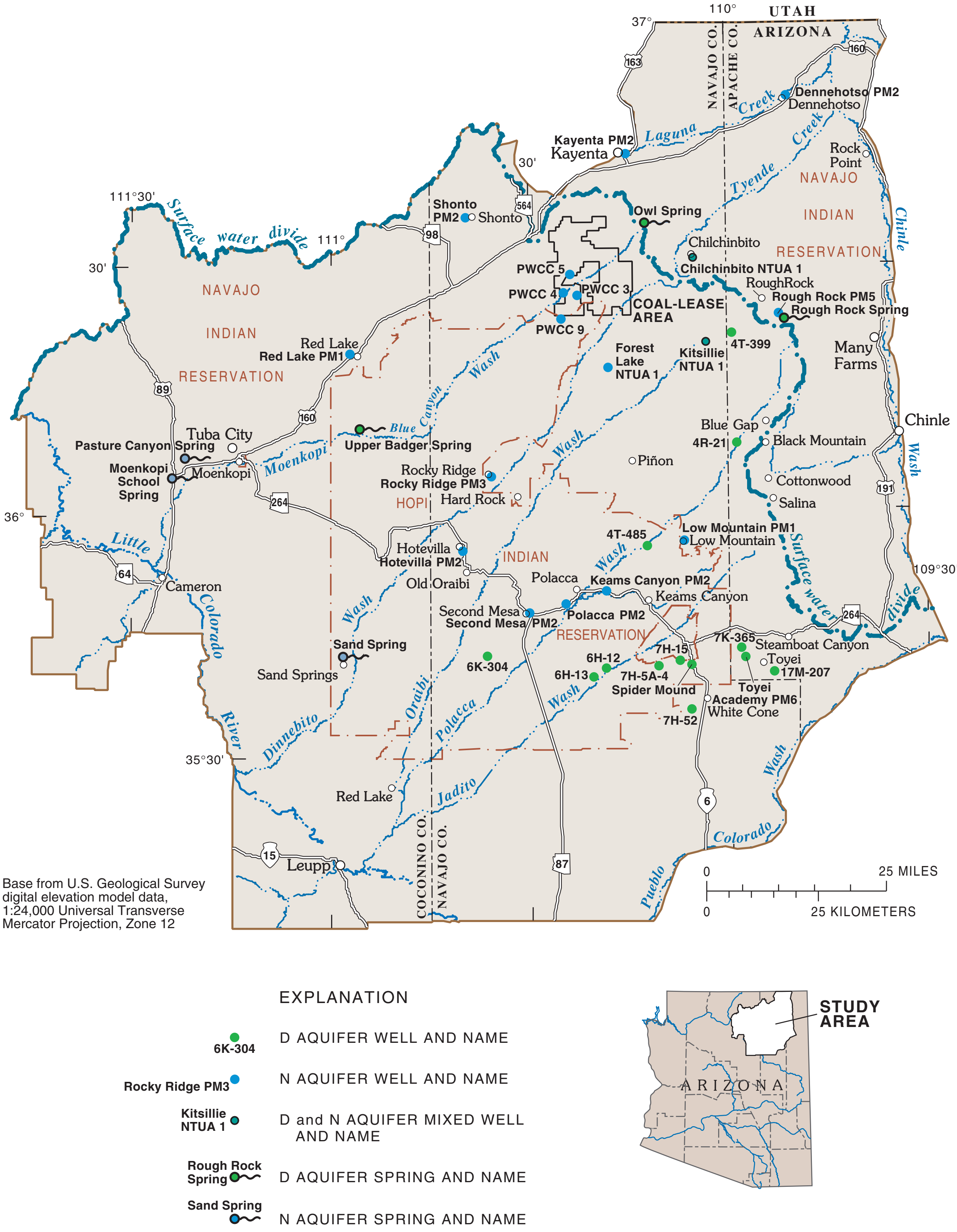


**Figure 1**. Location of study area and wells and springs sampled for ground-water chemistry analyses, Black Mesa area, northeastern Arizona.

**Table 1**. Laboratory analytes

[Note: analytes for spring samples were dependent on spring discharge; see table 3 for laboratory analyses]

| Major ions | Minor ions | Stable isotopes | Radioactive isotopes |
|---|---|---|---|
| **Water samples from D aquifer wells** | | | |
| Calcium | Boron | Oxygen-18/oxygen-16 | Carbon-14 |
| Sodium | Manganese | Hydrogen-2/hydrogen-1 | Hydrogen-3 (tritium) |
| Magnesium | Iron | Carbon-13/carbon-12 | |
| Potassium | Strontium | Boron-11/boron-10 | |
| Sulfate | Barium | Sulfur-34/sulfur-32 (sulfate) | |
| Chloride | Arsenic | Oxygen-18/oxygen-16 (sulfate) | |
| Fluoride | | Strontium-87/strontium-86 | |
| Dissolved silica ($H_4SiO_4$) | | | |
| **Water samples from N aquifer wells** | | | |
| None | None | Oxygen-18/oxygen-16 | [1]Carbon-14 |
| | | Hydrogen-2/hydrogen-1 | [1]Hydrogen-3 (tritium) |
| | | Carbon-13/carbon-12 | |
| | | Boron-11/boron-10 | |
| | | Sulfur-34/sulfur-32 (sulfate) | |
| | | Oxygen-18/oxygen-16 (sulfate) | |
| | | Strontium-87/strontium-86 | |
| **Rock samples** | | | |
| None | None | Oxygen-18/oxygen-16 (sulfate) | |
| | | Sulfur-34/sulfur-32 (sulfate) | |
| | | Carbon-13/carbon-12 | |
| | | Strontium-87/strontium-86 | |

[1] Selected wells only.

Raw, unfiltered water samples were collected for analyses of $^{18}O/^{16}O$, $^{2}H/^{1}H$, $^{18}O/^{16}O$ and $^{34}S/^{32}S$ from sulfate, $^{11}B/^{10}B$, $^{3}H$, and major anions. Samples for $^{18}O/^{16}O$ and $^{2}H/^{1}H$ analyses were collected in 60-milliliter glass bottles that were filled to the top and sealed to prevent evaporation. Water samples for carbon isotope analyses were collected by slowly filling 1-liter glass bottles from the bottom to avoid introducing air into the samples. Samples for $^{3}H$ analysis were collected in 1-liter polyethylene bottles. Samples for each analysis of $^{18}O/^{16}O$ and $^{34}S/^{32}S$ from sulfate were collected in two 250-milliliter polyethylene bottles. Water samples for $^{11}B/^{10}B$ analysis were collected in 250-milliliter polyethylene bottles. Alkalinity was measured on site using filtered aliquots.

Major and minor anions and carbon isotopes were analyzed at the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado. Analyses of $^{87}Sr/^{86}Sr$ were performed at a laboratory operated by Zell Peterman, research geologist with the USGS in Lakewood, Colorado, and at a laboratory operated by Thomas Bullen, research hydrologist with the USGS in Menlo Park, California. Analyses of $^{3}H$

were performed at the USGS laboratory in Menlo Park. Analyses of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ were performed at the USGS laboratory in Reston, Virginia. Analyses of $^{18}O/^{16}O$ and $^{34}S/^{32}S$ from sulfate were performed by Craig Johnson at a laboratory operated by Bob Rye, research geologist with the USGS in Denver. Analyses of $^{11}B/^{10}B$ were performed at a laboratory operated by Randy Bassett at the University of Arizona, Tucson.

Stable-isotope ratios are reported relative to internationally agreed upon standards. Deviations from standards are expressed in per mil (‰) using the delta (δ) notation:

$$\delta = \frac{R_x - R_{\text{std}}}{R_{\text{std}}} \times 1{,}000\,, \tag{1}$$

where

$\delta$ = delta value, in per mil (‰),

$R_x$ = ratio of isotopes in sample, such as $^{13}C/^{12}C$ or $^{18}O/^{16}O$, and

$R_{\text{std}}$ = ratio of isotopes in the standard.

The delta symbol in this report is followed by the chemical symbol for the heavier isotope measured during isotopic analysis. Isotopic values are described as lighter or heavier in relation to each other. Lighter isotopic values are smaller or more negative per mil values, and heavier isotopic values are larger or more positive per mil values.

Tritium ($^{3}H$) is reported in picocuries per liter (pCi/L) in this report. Natural background levels of $^{3}H$ in the atmosphere and ground water are about 5 tritium units or 16 pCi/L (Mazor, 1991; Clark and Fritz, 1997); however, anthropogenic $^{3}H$ was produced by atmospheric thermonuclear tests that began in 1952. Anthropogenic $^{3}H$ peaked in about 1963 before atmospheric testing was banned (Mazor, 1991; Clark and Fritz, 1997). Consequently, semiquantitative dating of ground water is possible. Water having less than 1.6 pCi/L was recharged before 1953; water having greater than 32 pCi/L typically can be assumed to have recharged after atmospheric thermonuclear testing began. Water having between 1.6 and 32 pCi/L is a mixture of pre- and post-bomb waters (Mazor, 1991; Clark and Fritz, 1997).

The geochemical mass-balance code NETPATH (Plummer and others, 1994) was used to adjust $^{14}C$ ages from analytical data. Several carbon-activity model routines that are written into the NETPATH code can be used to do so. The model routines, to varying degrees, consider processes including the exchange of dissolved inorganic carbon with soil-zone $CO_2$ and dilution of inorganic carbon by carbonate-mineral dissolution. These adjusted results are then compared to the measured $^{14}C$ activity through the radioactive-decay equation to determine the radiocarbon age of the water (Plummer and others, 1994):

$$t = \frac{5{,}730}{\ln 2} \ln\left(\frac{A_{nd}}{A_{meas}}\right), \tag{2}$$

where

$t$ = age or travel time, in years,

ln = natural logarithm,

$A_{nd}$ = initial $^{14}C$ activity, adjusted for reactions assuming no radioactive decay, and

$A_{meas}$ = measured $^{14}C$ activity at a point downgradient from the initial well.

This study used the model by Fontes and Garnier (1979). Inherent model assumptions are (1) a confined system, (2) a user-defined value for $\delta^{13}C$, which enables the user to input the initial $\delta^{13}C$ of soil $CO_2$, and (3) measured solid-phase (rock samples) $\delta^{13}C$ values.

## Statistical Analyses

The Kruskal-Wallis test (Helsel and Hirsch, 1992)—a nonparametric measure of the association between several independent sets of data—was used to test the null hypothesis that values of $^{87}Sr/^{86}Sr$, $\delta^{11}B$, and $\delta^{34}S$ from sulfate ($\delta^{34}S_{(\text{sulfate})}$) were not significantly different among (1) N aquifer ground water in the area apparently affected by leakage, (2) N aquifer ground water in other areas, and (3) D aquifer ground water. The null hypothesis of identical median values for all data sets was rejected if the probability of obtaining identical medians by chance was less than or equal to 0.05. If the null hypothesis of the Kruskal-Wallis test was rejected for any of the tests conducted, then the Tukey method of multiple comparisons was applied on the ranks of the data set (Helsel and Hirsch, 1992). This test was used to identify significant differences in $^{87}Sr/^{86}Sr$ values for each pairwise comparison. The null hypothesis of identical median values for each pairwise comparison was rejected if the probability of obtaining identical medians by chance was less than or equal to 0.05.

The Tukey method uses the harmonic mean of the group sample size to identify significant differences. If one group sample size is smaller than the other group sample size, the mean sample size is lowered and the smallest difference necessary to declare significance increases. Ranked data were used in both the Kruskal-Wallis test and the Tukey method because the raw data are not normally distributed.

## HYDROGEOLOGIC SETTING

Black Mesa is a large moderately dissected highland in the Black Mesa Basin. This basin filled with as much as several thousand feet of sediments from Cambrian to Tertiary time, over a period of about 570 million years. Deposition attendant to marine advances and retreats yielded complex, intertonguing lithologic units and abrupt facies changes. Highlands northeast of the study area were major sources of sediment during late Paleozoic and Early Triassic time, whereas the Mogollon Highlands, south of the area, continued to contribute sediments during the Jurassic and Cretaceous Periods (Cooley and others, 1969).

The basin was deformed during Late Cretaceous uplift, but less so than was the rest of the Colorado Plateau. The resultant deformation of the flat-lying sandstones, siltstones, and claystones induced structural features, including folds and faults, that together with the facies variations form some of the principal controls on the occurrence and movement of ground water in the study area (Cooley and others, 1969). The sedimentary sequence is amenable to delineation of three principal hydrostratigraphic units. These are, in order of increasing depth below land surface, the D, N, and C aquifers (Cooley and others, 1969).

### Geologic Units Overlying the D Aquifer

Geologic units overlying the D aquifer, from oldest to youngest, are the Mancos Shale and the Mesa Verde Group of Cretaceous age, the Bidahochi Formation of Tertiary age, volcanic rocks of late Cenozoic age, and unconsolidated surficial deposits of Quaternary age (figs. 2 and 3). In some parts of the study area, one or more of these units has been removed by erosion. The Mancos Shale consists of lower and upper parts; only the lower part is present in the Black Mesa area. This part is further subdivided into a lower shale unit, a limestone unit, and a medial shale unit (O’Sullivan and others, 1972). In all but the northeastern part of Black Mesa, the limestone unit is absent, and the medial shale unit is indistinguishable from the lower shale unit. The lower part of the Mancos intertongues with the overlying Toreva Formation of the Mesa Verde Group. In about the south half of Black Mesa, the Toreva consists of a basal cliff-forming sandstone member, a middle slope-forming carbonaceous member, and an upper cliff-forming sandstone member (O’Sullivan and others, 1972). In about the north half of Black Mesa, the Toreva consists of three units that are different from the members recognized in the south half of the mesa. The three units are a basal sandstone unit, a marine shale tongue, and a locally present upper cliff-forming sandstone. The Toreva grades into the overlying Wepo Formation, which comprises a thick series of intercalated siltstone, mudstone, sandstone, and coal (O’Sullivan and others, 1972; Eaton and others, 1988). The Wepo overlies most of Black Mesa and is mined for coal by the PWCC. The youngest unit in the Mesa Verde Group, the Yale Point Sandstone, intertongues with the underlying Wepo Formation and consists of fine- to medium-grained sandstone. The Yale Point forms the uppermost unit of Black Mesa in the northeastern part of the area where the formation is thickest (Repenning and Page, 1956). Stratigraphically above the Yale Point Sandstone is the Bidahochi Formation of Tertiary age, which consists of mudstones, muddy sandstones, rhyolitic ash, basalt, and a fine-grained silty sandstone (Shoemaker and others, 1962). The Bidahochi is overlain by volcanic rocks of late Cenozoic age and unconsolidated Quaternary sediments that include eolian, terrace, and landslide deposits, and alluvium (Cooley and others, 1969). The Quaternary sediments are discontinuous over the study area.

## Hydrogeologic Units of the D and N Aquifers

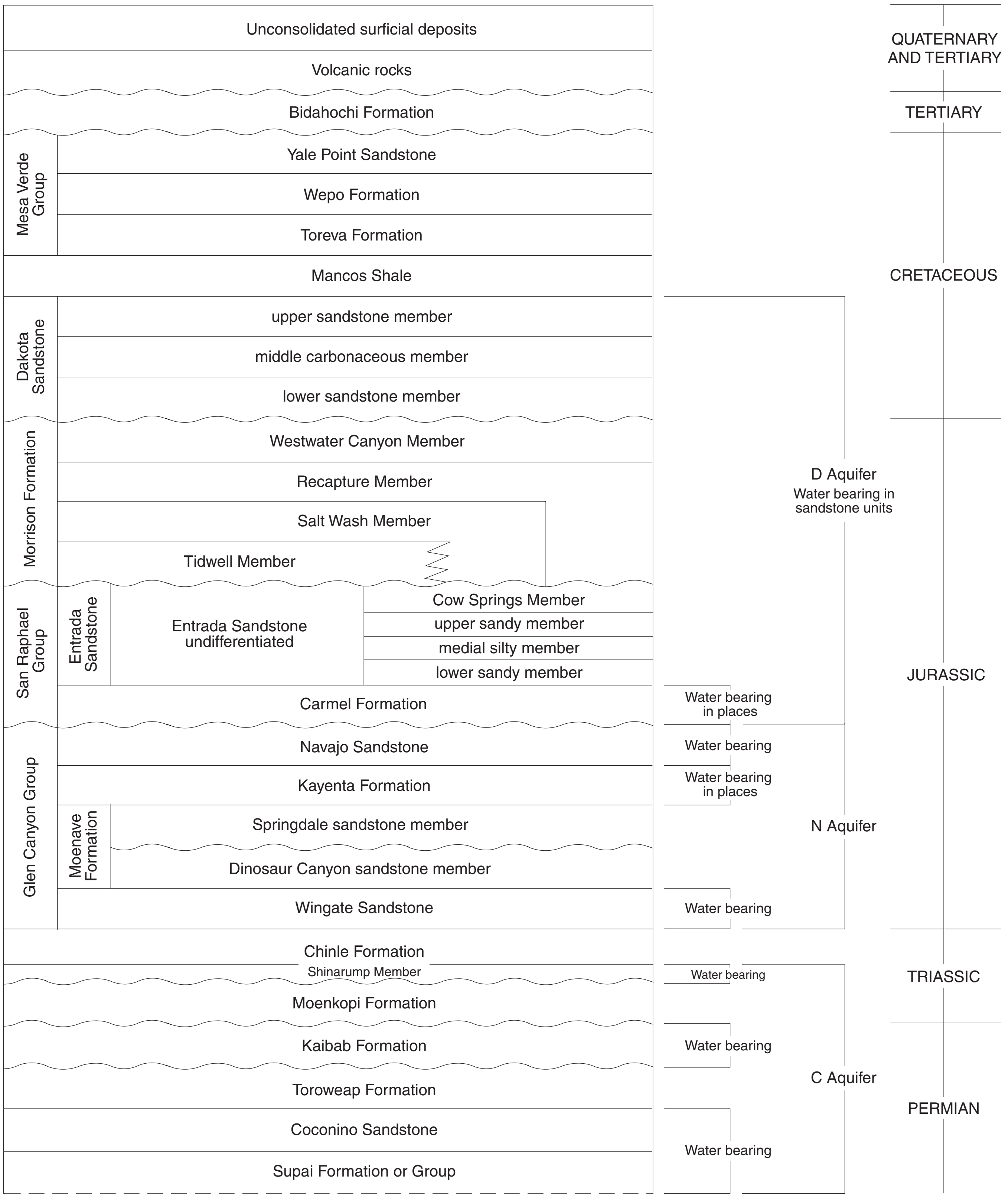
The D aquifer includes the Dakota Sandstone of Cretaceous age, the Morrison Formation of Jurassic age, the Entrada Sandstone of Jurassic age, and in the southeastern part of the study area the Carmel Formation of Jurassic age (**figs. 2** and **3**). The aquifer was named for the Dakota Sandstone, which is the primary water-bearing unit (Cooley and others, 1969). The lithology of most units varies in the study area as a result of variations in depositional processes. The units of the D aquifer are exposed around the perimeter of Black Mesa. The Dakota Sandstone is exposed on the southeastern, southwestern, and western edges of Black Mesa; the Morrison is exposed on the eastern and northeastern edges; the Entrada is exposed on the eastern, northeastern, western, and southwestern edges; and the Carmel is exposed on the western and southwestern edges (fig. 3).

The Dakota Sandstone has three distinct members—the upper sandstone member, the middle carbonaceous member, and the lower sandstone member (O'Sullivan and others, 1972). The three members were deposited in response to changes in the environment marginal to advancing Cretaceous seas; however, deposition throughout the Navajo country was irregular (O'Sullivan and others, 1972). The depositional irregularity means that any one of these units may be duplicated or absent at particular localities. The upper sandstone member, present in the northern part of Black Mesa and absent in most of the southwestern part, consists of alternating thin sandstone and intercalated shaly beds. The middle carbonaceous member is a siltstone that contains coal-bearing seams and interbedded sandstone lenses and gypsum stringers. The lower sandstone member is similar in composition to the upper sandstone member but is coarser grained. The lower sandstone member and some lenticular sandstone beds in the middle carbonaceous member have relatively high permeability. Permeability of the upper sandstone member is low owing to the high silt content (O'Sullivan and others, 1972).

The Morrison Formation in the Black Mesa area consists of four members—the Westwater Canyon, Recapture, Salt Wash, and Tidwell Members. The Westwater Canyon Member is a sandstone that contains minor mudstone and local stringers of pebble conglomerate. This member is composed, in general, of interstratified sandstones and shaly mudstones. The Recapture Member is thickest in northeastern Black Mesa and is absent in the southwestern part (Harshbarger and others, 1957). The Salt Wash Member consists of sandstone and minor mudstones (Peterson, 1988). Underlying the Salt Wash Member is the Tidwell Formation, a mudstone that interfingers with the Salt Wash Member in places (Peterson, 1988).

In the Black Mesa area, the Morrison Formation is underlain by units of the Entrada Sandstone. Four members of the Entrada have been identified in the area—the Cow Springs, upper sandy, medial silty, and lower sandy members (Harshbarger and others, 1957; Peterson, 1988). The Cow Springs Member is a light-colored crossbedded sandstone that is recognized on the northwest side, part of the east side, and the southeast side of Black Mesa. It is not present on the northeast and southwest sides of the basin. In these areas, units of the Morrison Formation are underlain by the lower part of the Entrada Sandstone (Peterson, 1988). The upper sandy member is present along the eastern edge of Black Mesa and is a medium- to fine-grained sandstone. The medial silty member is a very fine-grained sandstone. The lower contact of this unit is gradational with underlying units: the lower sandy member of the Entrada and the Carmel Formation. The medial silty member is absent in the western part of the study area (Harshbarger and others, 1957). The lower sandy member is similar in lithology to the upper sandy member but is present as a separate unit only in the central, northern, and northwestern parts of the study area. In the southwestern part of the study area, it consists of very fine sand and silt and cannot be separated from the underlying white sandy facies of the Carmel Formation (Harshbarger and others, 1957).

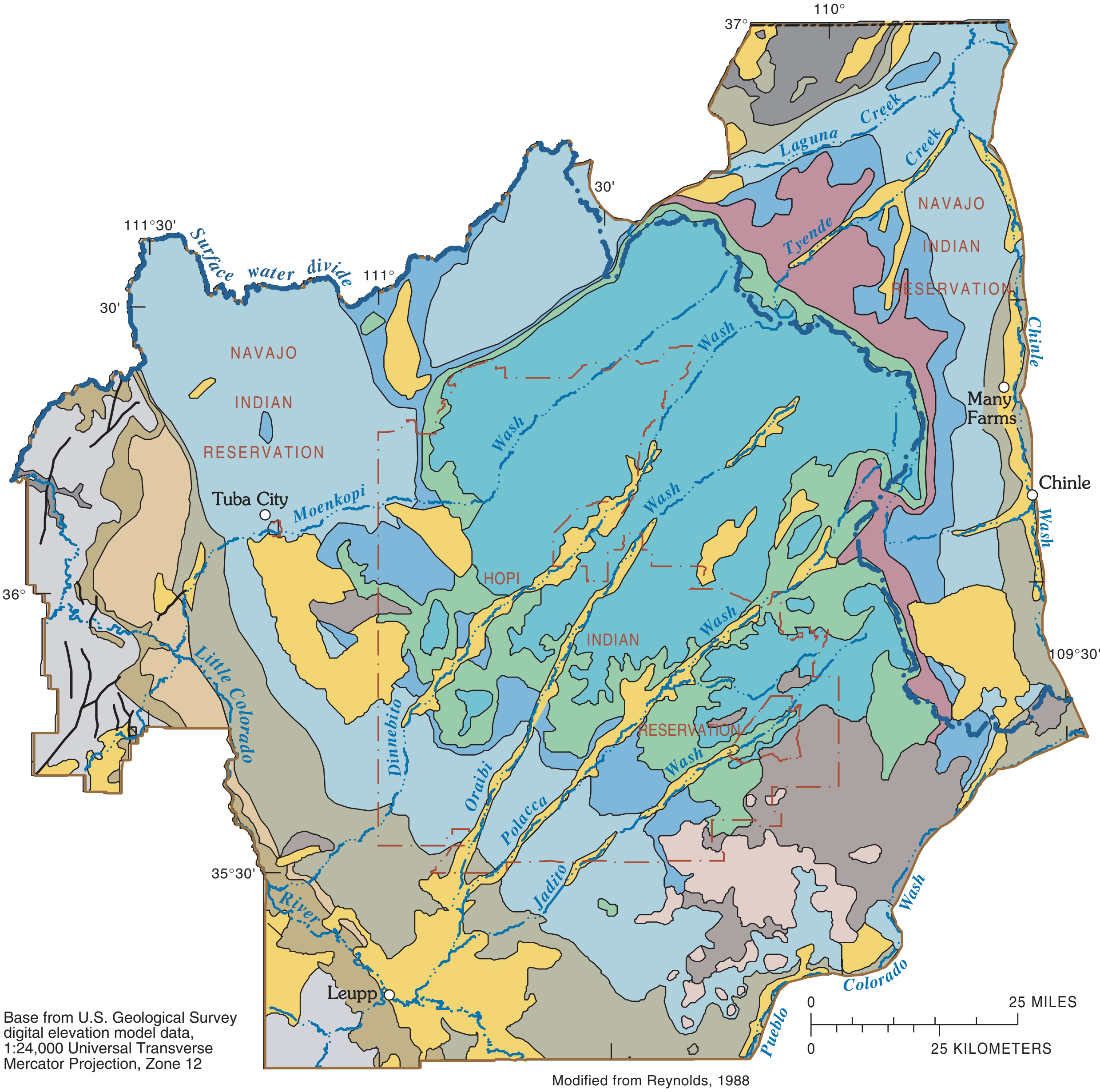
The Carmel Formation consists of a series of sandstone beds separated by siltstone beds (Harshbarger and others, 1957). In most of the study area, the sandstone beds are a minor part of the formation and the Carmel forms a confining unit between the D and N aquifers. The sandstone beds, however, thicken toward the southwest, and the lithology of the Carmel becomes indistinguishable from overlying units of the Entrada Sandstone (Harshbarger and others, 1957). West of the study area the Carmel yields water to springs (Cooley and others, 1969), and driller's logs from wells in the southwestern and southern parts of the study area indicate that the Carmel is a fine-grained, water-bearing sandstone.



**Note:** Members and units of formations underlying rocks of the N aquifer and overlying rocks of the D aquifer are not shown.

Geology from Harshbarger and others, 1957; Cooley and others, 1969; Irwin and others, 1971; O'Sullivan and others, 1972; Peterson and Pipiringos, 1979; Peterson, 1988; and Dubiel, 1989

**Figure 2.** Rock formations and hydrogeologic units of the D, N, and C aquifers, Black Mesa area, northeastern Arizona.



Base from U.S. Geological Survey digital elevation model data, 1:24,000 Universal Transverse Mercator Projection, Zone 12

Modified from Reynolds, 1988

**Figure 3**. Surface geology, Black Mesa area, northeastern Arizona.

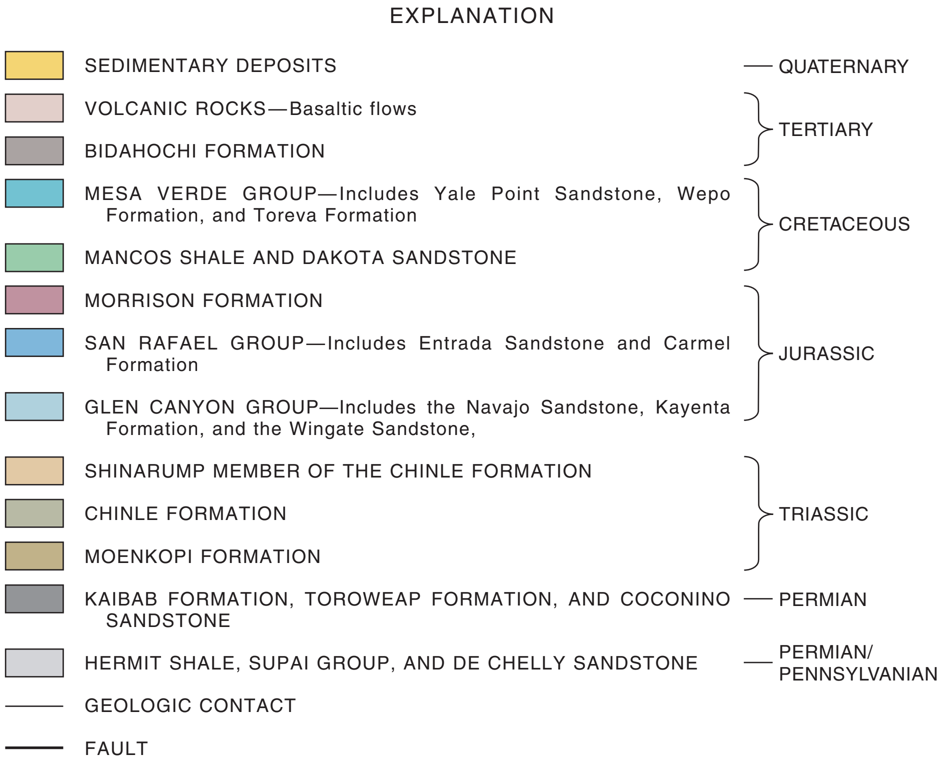


**Figure 3**. Continued.

For this reason, the undifferentiated Entrada and the Carmel are included in the D aquifer in these areas. South of Blue Canyon, the Carmel cannot be separated with any reliability from the Entrada (Harshbarger and others, 1957).

The N aquifer is the primary aquifer in the Black Mesa area (Lopes and Hoffmann, 1997). It is a multiple-aquifer system that encompasses several formations and heterogeneities within the formations (Cooley and others, 1969). The N aquifer consists of the Navajo Sandstone of Jurassic age, the Kayenta Formation of Triassic age, and the Wingate Sandstone of Late Triassic or Early Jurassic age (Cooley and others, 1969; Dubiel, 1989).

The Navajo Sandstone is the principle lithologic unit of the N aquifer and is a fine- to medium-grained, weakly-cemented, crossbedded sandstone that contains lenticular beds of cherty limestone. It lies beneath an unconformity at the base of the Carmel Formation (Harshbarger and others, 1957; Cooley and others, 1969). The N aquifer is about 1,000 ft thick at the northwest edge of Black Mesa and thins southeastward to extinction near Keams Canyon, Arizona (Eychaner, 1983; fig. 4).

The Kayenta Formation consists of two facies. One is a fine-grained sandstone interbedded with mudstones. This facies grades into an intercalated siltstone, mudstone, and sandstone sequence (silty facies) in the southwestern part of the study area (Harshbarger and others, 1957). The Kayenta interfingers with the overlying Navajo Sandstone throughout the study area, and the formation pinches out east and southeast of Black Mesa (Harshbarger and others, 1957). In the southwestern part of the study area, the Kayenta Formation acts as a confining bed that separates water in the Navajo Sandstone from that in the Wingate Sandstone. In the north-central part of the area, the sandy facies of the Kayenta Formation provides hydraulic connection between water in the Navajo Sandstone and water in the Wingate Sandstone. In the part of the study area southwest of a line that extends from near Steamboat Canyon to near Kayenta, the Moenave Formation of Triassic(?) age (Harshbarger and others, 1957) lies between the Kayenta Formation and the Wingate Sandstone. Units of the Moenave, however, are primarily sandy siltstone and silty sandstone that are not water bearing (Cooley and others, 1969).

The Wingate Sandstone in the Black Mesa area was subdivided by Harshbarger and others (1957) into the Lukachukai and Rock Point members. Dubiel (1989), however, recognized the unit referred to as the Rock Point member as a unit of the underlying Chinle Formation and abandoned the name Lukachukai in favor of the name Wingate for the sole remaining unit of the formation. The Wingate Formation is present in all but the extreme western and southeastern parts of the study area. It is a fine- to very fine-grained, crossbedded sandstone in most of the study area. Near Kayenta, the base of the formation is a conglomeratic sandstone (Beaumont and Dixon, 1965). The Wingate intertongues with the overlying Moenave Formation where the two units are present.

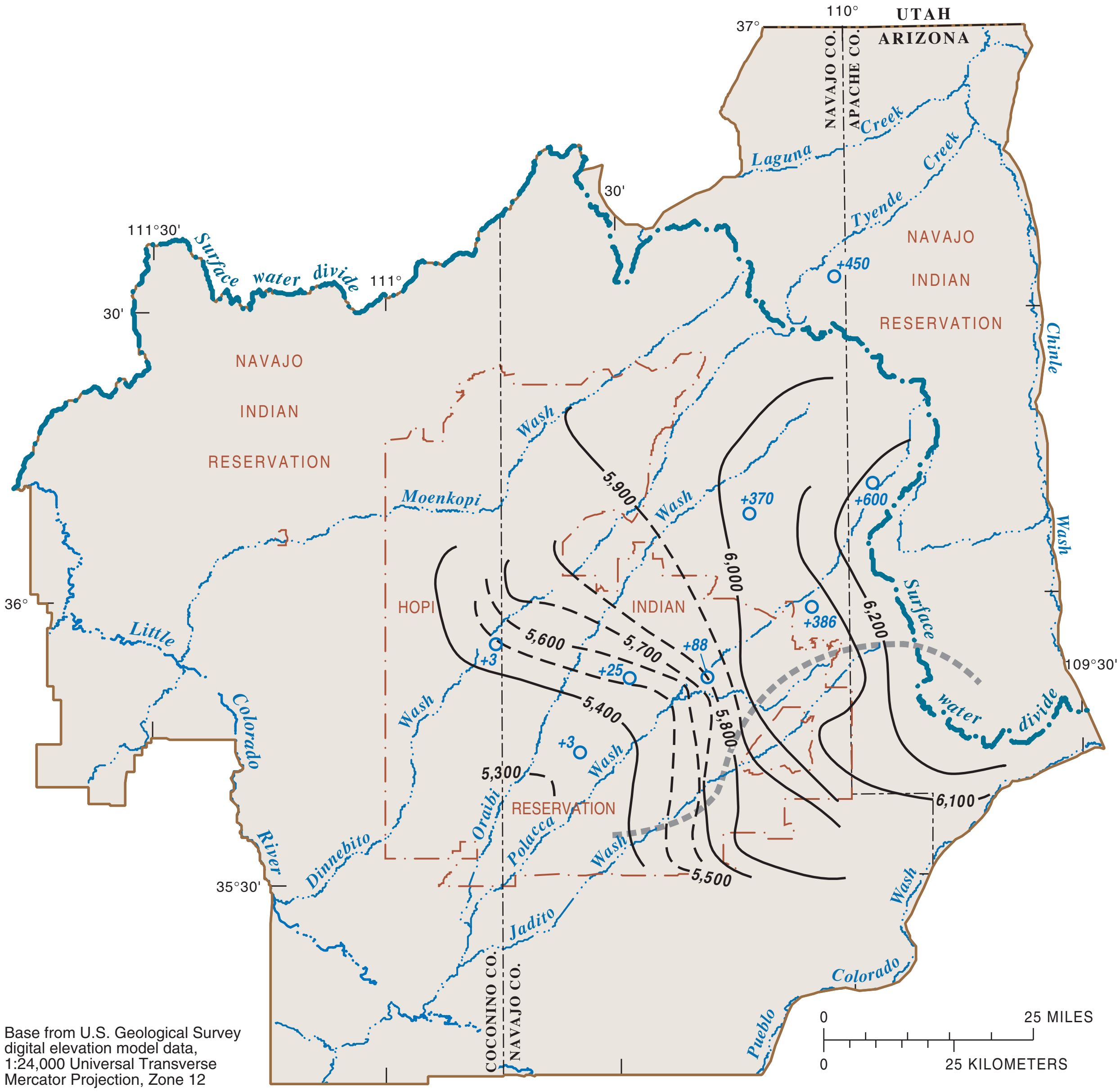
### Ground-Water Conditions in the D Aquifer

Ground-water conditions in the D aquifer are controlled in part by the lithology of the rock units that make up the aquifer and the lithology of the units that lie stratigraphically above and below the aquifer. Ground water that can be withdrawn by wells occurs in formations that are chiefly sandstone and in parts of formations or formation members that contain sandstone beds or lenses. In most of the study area, the Mancos Shale is a confining unit above the D aquifer. The aquifer receives recharge from precipitation and ephemeral streams in areas where aquifer units are exposed or are covered by a veneer of unconsolidated sediments. Ground water generally flows south and southwest toward the flood-plain alluvium along tributaries to the Little Colorado River (Cooley and others, 1969).

On the basis of water-level data from 1951 to 1961, the potentiometric surface of the D aquifer ranges in altitude from about 6,200 ft on the eastern edge of Black Mesa to about 5,200 ft on the southwestern edge (**fig. 4**). Current (2003) water levels are believed to be similar because there are no known large-scale withdrawals from wells completed in the D aquifer. In most of the Black Mesa area, ground-water levels in the D aquifer are higher than ground-water levels in the N. In the area of the Hopi Mesas, ground-water levels in the two aquifers are about the same (fig. 4). Differences in the potentiometric surfaces using N aquifer prestress water levels (Thomas, 2002) indicate ground-water levels in the D aquifer are about 250 ft higher than levels in the N aquifer near PWCC, about 450 ft higher near the Forest Lake Chapter House, about 370 ft higher near Piñon, and decline to near zero on the southwestern edge of Black Mesa (fig. 4). In the southeastern part of Black Mesa, the N aquifer is thin and the hydraulic gradient and lateral flow rates are small (Eychaner, 1983). Geochemical evidence of leakage would be most apparent in this area. The vertical hydraulic gradient might also cause leakage in areas where any geochemical effects would be obscured by dilution because of greater thickness or more rapid flow in the N aquifer.

## GEOCHEMICAL EVOLUTION OF GROUND WATER IN THE D AQUIFER

Variations in ground-water chemistry along flow paths are controlled by aquifer mineralogy, geochemical processes, and grain-size distributions, which differ among the various geologic units of the D aquifer. The number of wells available for sampling along a specific flow path, however, is small, and the wells are open to different intervals in the aquifer (**table 2**). Thus, a geochemical analysis of water from each well must consider the uncertainty of a specific flow path within the aquifer as well as the potential effects from leakage. Grouping the data by nominal aquifer and by general location can introduce variability resulting from distinct hydrogeochemical processes.



Base from U.S. Geological Survey
digital elevation model data,
1:24,000 Universal Transverse
Mercator Projection, Zone 12

EXPLANATION

——— *6,000* — — POTENTIOMETRIC CONTOUR—Shows the altitude at which the water level would have stood in a tightly cased well, 1951–61, in feet above mean sea level. Dashed where approximately located. Contour interval 100 feet

▪▪▪▪▪▪▪▪ APPROXIMATE SOUTHEAST LIMIT OF THE NAVAJO SANDSTONE

*+370* ○ DIFFERENCE BETWEEN POTENTIOMETRIC SURFACE OF THE D AQUIFER AND PRESTRESS WATER LEVEL IN THE N AQUIFER—in feet. Data for N aquifer from Thomas (2002).

**Figure 4**. Potentiometric surface of the D aquifer, 1951–61, and difference between potentiometric surface and prestress water levels in the N aquifer, Black Mesa area, northeastern Arizona.

**Table 2.** Lithology, water levels, and open-interval data for D aquifer wells used for ground-water chemistry analyses, Black Mesa area, northeastern Arizona

| Well name | Altitude (feet above sea level) | Formation name | Water level (feet above sea level) | Date measured | Open interval (feet above sea level) |
|---|---|---|---|---|---|
| 4R-21 | 6,420–6,330 | Alluvium | 6,240 | 1954 | Open hole 6,111–6,035 |
|  | 6,330–6,153 | Morrison Formation |  |  |  |
|  | 6,153–6,035 | Entrada Sandstone |  |  |  |
| 4T-399 | 6,841–6,611 | Alluvium | 6,057 | 1958 | Perforated from 5,843–5,669 |
|  | 6,611–6,261 | Toreva Sandstone |  |  |  |
|  | 6,261–5,843 | Mancos Shale |  |  |  |
|  | 5,843–5,669 | Dakota Sandstone |  |  |  |
| 4T-485 | 6,486–6,396 | Wepo Formation | 6,014 | 1954 | Perforated from 5,544–5,475 |
|  | 6,396–6,036 | Toreva Sandstone[2] |  |  |  |
|  | 6,036–5,556 | Mancos Shale |  |  |  |
|  | 5,556–5,469 | Dakota Sandstone |  |  |  |
| 6H-12 | 5,782–5,697 | Alluvium | 5,720 | 1999 | Perforated from 5,732–5,612 |
|  | 5,697–5,588 | Dakota Sandstone[2] |  |  |  |
| 6H-13 | 5,707–5,636 | Alluvium | 5,579 | 1999 | Perforated from 5,623–5,386 |
|  | 5,636–5,357 | Entrada Sandstone |  |  |  |
| 6K-304 | 5,485–5,480 | Alluvium | 5,342 | 1999 | Perforated from 5,345–5,285 |
|  | 5,480–5,297 | Entrada Sandstone |  |  |  |
|  | 5,297–5,285 | Carmel Sandstone |  |  |  |
| 7H-5A-4 | 6,267–6,157 | Toreva | 5,970 | 1976 | Perforated from 5,741–5,593 |
|  | 6,157–5,707 | Mancos Shale |  |  |  |
|  | 5,707–5,593 | Dakota Sandstone[2] |  |  |  |
| 7H-15 | 6,676–6,672 | Alluvium | 5,955 | 1936 | Open hole |
|  | 6,672–6,286 | Bidahochi Formation |  |  |  |
|  | 6,286–5,791 | Mancos Shale |  |  |  |
|  | 5,791–5,683 | Dakota Sandstone |  |  |  |
| 7H-52 | 6,042–6,032 | Alluvium | [1]5,765 | 1934 | Open hole |
|  | 6,032–5,962 | Bidahochi Formation |  |  |  |
|  | 5,962–5,762 | Mancos Shale |  |  |  |
|  | 5,762–5,618 | Dakota Sandstone |  |  |  |
| 7K-365 | 6,452–6,352 | Alluvium | 6,165 | 1955 | Perforated from 6,047–5,982 |
|  | 6,352–6,246 | Bidahochi Formation |  |  |  |
|  | 6,246–6,062 | Mancos Shale |  |  |  |
|  | 6,062–5,908 | Dakota Sandstone[2] |  |  |  |
| 17M-207 | 6,164–6,140 | Alluvium | 6,125 | 1954 | Screened 10 ft. Probably from 5,965–5,955 |
|  | 6,140–6,068 | Bidahochi Formation |  |  |  |
|  | 6,068–6,040 | Dakota Sandstone |  |  |  |
|  | 6,040–5,955 | Morrison Formation |  |  |  |
| Spider Mound | 6,653–6,543 | Bidahochi Formation | 6,113 | 1994 | Open hole from 5,788–4,853 |
|  | 6,543–6,253 | Mesa Verde |  |  |  |
|  | 6,253–5,843 | Mancos Shale |  |  |  |
|  | 5,843–5,483 | Dakota Sandstone |  |  |  |
|  | 5,483–4,853 | Entrada/Carmel Formation |  |  |  |
| Toyei Academy PM6 | [3]6,565–6,415 | Bidahochi Formation | 6,155 | 1967 | Open hole 6,033–5,907 |
|  | [3]6,415–6,033 | Mancos Shale |  |  |  |
|  | 6,033–5,907 | Dakota Sandstone |  |  |  |

[1] Approximate water level.

[2] Coal (lignite) bearing.

[3] Estimated.

Water-rock reactions described for the D aquifer in the southern part of the Black Mesa area are assumed to be similar to reactions occurring in other parts of the aquifer. The ground-water evolution in the D aquifer is similar to that occurring in the N aquifer (Lopes and Hoffmann, 1997); however, some of the geochemical processes and minerals contributing to the D aquifer ground-water chemistry are different from geochemical processes and minerals in the N aquifer. Reactions involved in ground-water evolution in the D aquifer are weak-acid/strong-base reactions and dissolution/precipitation of primary and secondary aquifer minerals.

Water-rock reactions in the D aquifer occur as water moves downgradient and are responsible for constituents dissolved in the ground water. Thin-section analysis revealed that rocks within the Dakota Sandstone and the Entrada and Carmel Formations contain alkali and plagioclase feldspars, clays, iron oxides, chert, and calcium-carbonate cement (GeoTrans, Inc., 1993). Drillers' logs indicated the presence of lignite seams within the Dakota Sandstone (**table 2**).

The following simplified equation describes the reaction that takes place during silicate hydrolysis:

$$\text{Feldspar minerals} + CO_2 + H_2O = \text{cations}_{(aq)} + H_4SiO_{4(aq)} + HCO_3^-$$

$$+ \text{secondary minerals } (CaCO_3\text{, clays, amorphous } SiO_2) + OH^- . \qquad (3)$$

Dissolution of a feldspar contributes calcium, sodium, potassium, aluminum, and silicon into solution (Holdren and Speyer, 1986). The initial composition of a feldspar can also influence the compositions of the secondary mineral phases such as clays. The exchange of $Ca^+$ for $Na^+$ in the clays and lignites (Chapelle, 2001) will in part contribute toward a sodium bicarbonate type water along the flow path (**fig. 5**).

Two sources of dissolved sulfate—gypsum stringers and lignite seams—are known to exist in the Dakota Sandstone. Sulfate concentrations and $\delta^{34}S_{(sulfate)}$ values vary along the flow path, indicating water-rock interactions as well as microbial reduction are processes affecting the sulfur. Gypsum is present in the overlying Bidahochi Formation, Wepo Formation, and Mancos Shale, and gypsum dissolution (equation 4) appears to be contributing dissolved sulfate to ground water in the D aquifer at wells 6K-304, 7K-365, and Toyei Academy PM6 (**fig. 6**):

$$CaSO_4 \bullet 2H_2O + H_2O = Ca^{2+} + SO_4^{2-} + 3H_2O. \qquad (4)$$

Sulfate in wells 7K-365, Toyei Academy PM6, 7H-5A-4, and 6H-12 (fig. 6 and **table 3**) could also result from ground water interacting with lignite seams. $\delta^{34}S_{(sulfate)}$ values suggest microbial reduction of sulfate has occurred in ground water downgradient from these sites. The lignite will provide a source of organic carbon for the microbes as well as an initial source of sulfate:

$$2CH_2O + SO_4^{2-} + H_2O = H_2S + 2HCO_3^- + 2OH^-. \qquad (5)$$

Lithologic descriptions for wells 7K-365, 7H-5A-4, and 6H-12 indicate that lignite seams are present in the sediments. Sulfur isotopic values from ground water at wells 7K-365 (-6.4 ‰) and Toyei Academy PM6 (-2.8 ‰) are light. Ground water downgradient from these wells, at Spider Mound well and well 7H-15, contains heavier $\delta^{34}S_{(sulfate)}$ values (2.7 ‰ and 2.5 ‰, respectively) and lower concentrations of sulfate, indicating that sulfate reduction is occurring along this flow path (table 3). Farther along the flow path, at wells 7H-5A-4 and 6H-12, $\delta^{34}S_{(sulfate)}$ values become lighter (-7.7 ‰ and -7.1 ‰, respectively) and concentrations of sulfate increase. Downgradient from these wells, at well 6H-13, the $\delta^{34}S_{(sulfate)}$ value becomes heavier (0.9 ‰) and the sulfate concentration decreases. Regardless of the source of sulfate, microbial reduction appears to be occurring. The reaction shown in equation 5 is supported by data plotted in **figure 7**, in which bicarbonate concentration increases in areas where sulfate is being reduced. The increase in bicarbonate contributes to the formation of calcite.

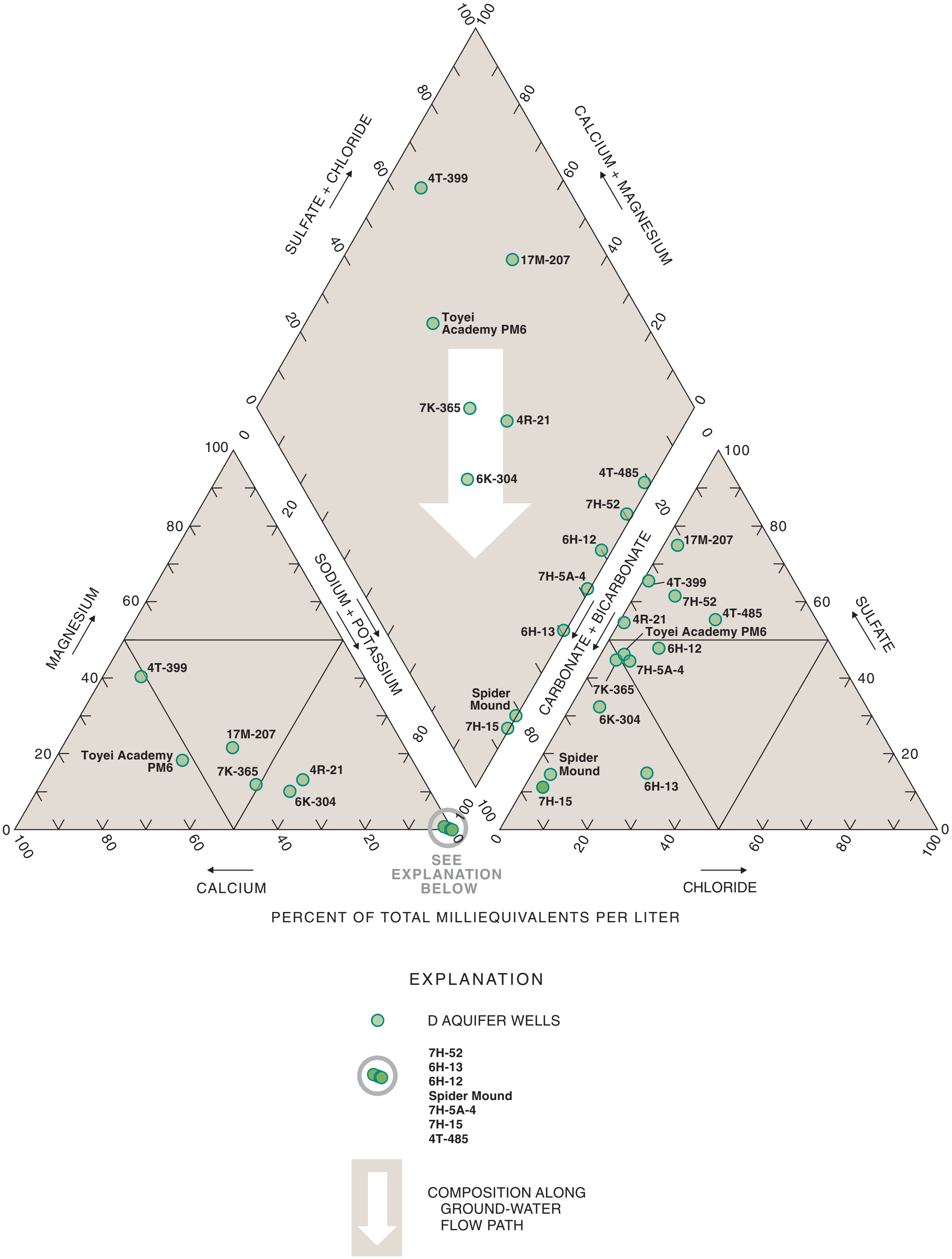


**Figure 5.** Relative compositions of water from the D aquifer, Black Mesa area, northeastern Arizona.

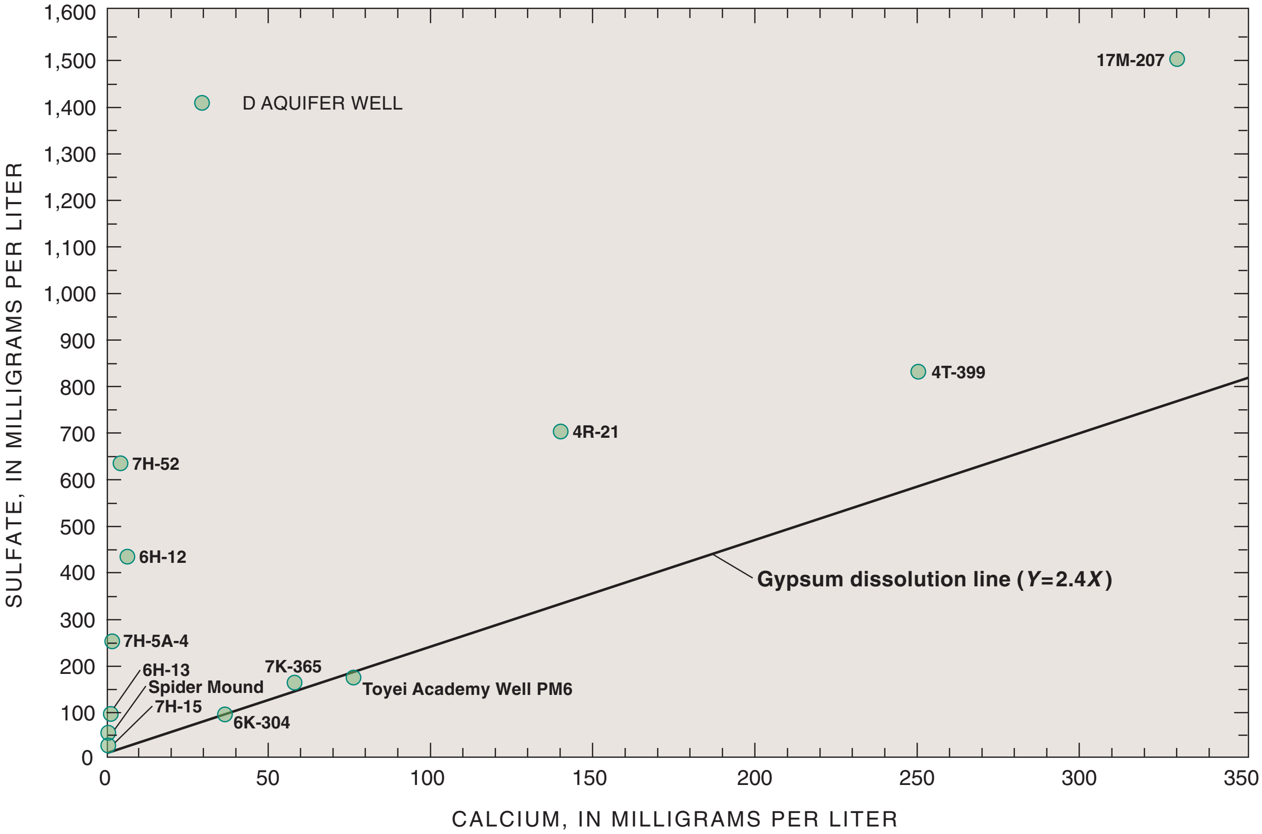


**Figure 6**. Relation between calcium and sulfate concentrations and the gypsum dissolution line in water from the D aquifer, Black Mesa area, northeastern Arizona.

**Table 3**. Inorganic and isotope data for the D and N aquifers, Black Mesa area, northeastern Arizona

[---, dashes indicate no data; mg/L, milligrams per liter; µS/cm, microseimens per centimeter at 25 degrees Celsius; Mix, mixture of D and N aquifer ground water; D, D aquifer; N, N aquifer; µg/L, micrograms per liter; <, less than; pCi/L, picocurries per liter; pmc, percent modern carbon]

| Well or spring name | Site identifier | Date sampled | Aquifer unit | Water temperature (degrees Celsius) | Specific conductance, field (µS/cm) | Dissolved oxygen (mg/L) | pH, field (standard units) | Alkalinity (mg/L) |
|---|---|---|---|---|---|---|---|---|
| Chilchinbito NTUA 1 | 363122110042701 | 19980804 | Mix | 18.1 | 1,580 | 0.5 | 8.7 | 130 |
| Kitsillie NTUA 1 | 362035110032201 | 19980827 | Mix | 23.5 | 1,550 | 1.3 | 8.9 | 220 |
| Rough Rock PM5 | 362418109512601 | 19971210 | Mix | 19.5 | 1,060 | 1.6 | 9.1 | 222 |
| 4R-21 | 360826109584001 | 19990812 | D | 14.9 | 2,140 | 3.3 | 7.4 | 480 |
| 4T-399 | 362150109591801 | 19990811 | D | 15.6 | 1,870 | .7 | 7.2 | 360 |
| 4T-485 | 355548110121801 | 19990811 | D | 19.2 | 1,890 | .6 | 8.7 | 150 |
| 6H-12 | 354058110182501 | 19990727 | D | 21.8 | 1,890 | 5.9 | 8.6 | 330 |
| 6H-13 | 353959110203701 | 19990720 | D | 19.1 | 1,200 | .1 | 9.3 | 350 |
| 6K-304 | 354227110362701 | 19990728 | D | 18.2 | 564 | 3.9 | 8.0 | 150 |
| 7H-5A-4 | 354122110103901 | 19990722 | D | 22.1 | 1,230 | 6.4 | 8.8 | 270 |
| 7H-15 | 354153110072601 | 19990721 | D | 19.5 | 441 | 5.0 | 9.0 | 220 |
| 7H-52 | 353551110054801 | 19990729 | D | 16.0 | 2,220 | 1.1 | 8.7 | 300 |
| 7H-365 | 354324109581801 | 19990810 | D | 17.8 | 663 | 1.1 | 8.2 | 160 |
| 17M-207 | 354030109532801 | 19990810 | D | 14.9 | 3,340 | 1.1 | 7.1 | 460 |
| Owl Spring | 363504110093701 | 20000404 | D | 11.1 | 363 | --- | 8.0 | --- |
| Rough Rock Spring | 362410109521201 | 19960813 | D | 16.2 | 316 | --- | 8.5 | --- |
| Spider Mound | 354122110054001 | 19990728 | D | 21.0 | 605 | .3 | 8.8 | 280 |
| Toyei Academy PM6 | 354214109573801 | 19990813 | D | 18.3 | 768 | .4 | 7.5 | 150 |
| Upper Badger Spring | 360239110515801 | 20000406 | D | 11.6 | 1,026 | --- | 7.7 | --- |
| Dennehotso PM2 | 365045109504001 | 19971209 | N | 13.7 | 305 | 8.2 | 8.9 | 100 |
| Forest Lake NTUA 1 | 361737110180301 | 19980825 | N | 27.6 | 525 | 3.2 | 9.4 | 172 |
| Hotevilla PM2 | 355518110400301 | 19971216 | N | 24.5 | 295 | 6.4 | 9.6 | 120 |
| Kayenta PM2 | 364344110151201 | 19981201 | N | 15.5 | 349 | 5.6 | 8.0 | 110 |
| Keams Canyon PM2 | 355023110182701 | 19971209 | N | 18.7 | 1,040 | 8.2 | 9.2 | 300 |
| Low Mountain PM1 | 355633110064901 | 19960815 | N | 20.1 | 576 | .0 | 9.0 | 945 |
| Moenkopi Spring | 360632111131101 | 19981208 | N | 17.2 | 296 | --- | 7.4 | 97 |
| Pasture Canyon Spring | 361021111115901 | 19960815 | N | 17.0 | --- | 4.7 | 7.6 | --- |
| Polacca PM2 | 354848110243401 | 19980828 | N | 22.0 | 777 | 1.0 | 9.6 | 150 |
| PWCC 3 | 362625110223701 | 19930128 | N | 31.0 | 177 | 4.9 | 9.1 | 78 |
| PWCC 4 | 362647110243501 | 19971210 | N | 32.0 | 203 | 7.1 | 9.4 | 84 |
| PWCC 5 | 362901110234101 | 19930128 | N | 25.3 | 257 | 4.8 | 9.3 | 105 |
| PWCC 9 | 362333110250001 | 19930128 | N | 32.0 | 157 | 5.5 | 8.8 | 73 |
| Red Lake PM1 | 361933110565001 | 19971211 | N | 8.7 | 156 | 10.2 | 8.7 | 84 |
| Rocky Ridge PM3 | 360422110353501 | 19981204 | N | 11.2 | 222 | 6.2 | 9.9 | 110 |
| Sand Spring | 361011110554401 | 19931013 | N | 20.8 | 358 | 5.6 | 7.5 | 93 |
| Second Mesa PM2 | 354749110300101 | 19971211 | N | 19.0 | 646 | .8 | 9.9 | 250 |
| Shonto PM2 | 363558110392501 | 19881118 | N | 14.0 | 285 | --- | 7.8 | [1]101 |

See footnotes at end of table.

**Table 3**. Inorganic and isotope data for the D and N aquifers, Black Mesa area, northeastern Arizona—Continued

| Well or spring name | Site identifier | Date sampled | Calcium (mg/L) | Magnesium (mg/L) | Sodium (mg/L) | Potassium (mg/L) | Chloride (mg/L) | Sulfate (mg/L) |
|---|---|---|---|---|---|---|---|---|
| Chilchinbito NTUA 1 | 363122110042701 | 19980804 | 12.2 | 3.3 | 323 | 3.6 | 14.7 | 573 |
| Kitsillie NTUA 1 | 362035110032201 | 19980827 | 3.4 | .5 | 330 | 2.2 | 8.5 | 487 |
| Rough Rock PM5 | 362418109512601 | 19971210 | 3.3 | .3 | 230 | 9.4 | 130 | 112 |
| 4R-21 | 360826109584001 | 19990812 | 141 | 41.0 | 335 | 12.4 | 11.7 | 695 |
| 4T-399 | 362150109591801 | 19990811 | 249 | 116 | 47.5 | 8.6 | 11.5 | 831 |
| 4T-485 | 355548110121801 | 19990811 | 3.94 | 1.01 | 459 | 1.9 | 124 | 414 |
| 6H-12 | 354058110182501 | 19990727 | 6.1 | 2.0 | 399 | 2.4 | 82.1 | 427 |
| 6H-13 | 353959110203701 | 19990720 | 1.2 | .3 | 278 | .9 | 119 | 94 |
| 6K-304 | 354227110362701 | 19990728 | 36.3 | 7.0 | 73.5 | 2.6 | 13.9 | 93.9 |
| 7H-5A-4 | 354122110103901 | 19990722 | 1.4 | .3 | 265 | 1.0 | 30.2 | 253 |
| 7H-15 | 354153110072601 | 19990721 | .3 | .1 | 121 | .6 | 7.4 | 27 |
| 7H-52 | 353551110054801 | 19990729 | 4.4 | 1.3 | 497 | 6.3 | 69.1 | 634 |
| 7K-365 | 354324109581801 | 19990810 | 58.0 | 10.9 | 82.9 | 1.5 | 11.1 | 155 |
| 17M-207 | 354030109532801 | 19990810 | 334 | 108 | 365 | 4.0 | 47.1 | 1,540 |
| Owl Spring | 363504110093701 | 20000404 | --- | --- | --- | --- | --- | --- |
| Rough Rock Spring | 362410109521201 | 19960813 | 33.0 | 7.7 | 6.4 | --- | --- | --- |
| Spider Mound | 354122110054001 | 19990728 | .5 | .1 | 157 | .8 | 11.1 | 51.4 |
| Toyei Academy PM6 | 354214109573801 | 19990813 | 75.9 | 15.8 | 48.3 | 2.9 | 14.4 | 174 |
| Upper Badger Spring | 360239110515801 | 20000406 | --- | --- | --- | --- | --- | --- |
| Dennehotso PM2 | 365045109504001 | 19971209 | 8.0 | 1.91 | 58 | 5.8 | 10.9 | 14.3 |
| Forest Lake NTUA 1 | 361737110180301 | 19980825 | .7 | .1 | 101 | .7 | 23.7 | 53.8 |
| Hotevilla PM2 | 355518110400301 | 19971216 | 1.3 | .1 | 65.1 | .5 | 1.5 | 5.2 |
| Kayenta PM2 | 364344110151201 | 19981201 | 39.8 | 6.5 | 23 | 1.2 | 3.6 | 71 |
| Keams Canyon PM2 | 355023110182701 | 19971209 | 0.8 | 0.2 | 219 | .7 | 95.8 | 33.5 |
| Low Mountain PM1 | 355633110064901 | 19960815 | 2.5 | .6 | 380 | --- | 23.0 | 460 |
| Moenkopi Spring | 360632111131101 | 19981208 | 29.3 | 6.5 | 24.9 | 1.3 | 17.6 | 23.7 |
| Pasture Canyon Spring | 361021111115901 | 19960815 | 27.0 | 4.0 | 12 | --- | 5.0 | 17 |
| Polacca PM2 | 354848110243401 | 19980828 | .5 | .1 | 169 | .6 | 26.1 | 18.4 |
| PWCC 3 | 362625110223701 | 19930128 | 3.1 | .04 | 56 | .8 | 4.2 | 19 |
| PWCC 4 | 362647110243501 | 19971210 | 4.6 | .03 | 41 | 4.6 | 3.5 | 12 |
| PWCC 5 | 362901110234101 | 19930128 | 3.6 | .03 | 37 | .6 | 2.3 | 4.8 |
| PWCC 9 | 362333110250001 | 19930128 | 3.7 | .03 | 33 | .6 | 1.7 | 2.9 |
| Red Lake PM1 | 361933110565001 | 19971211 | 19.2 | 5.0 | 5.8 | .9 | 3.2 | 1.7 |
| Rocky Ridge PM3 | 360422110353501 | 19981204 | 1.0 | .1 | 54.8 | .4 | 3.2 | 5 |
| Sand Spring | 361011110554401 | 19931013 | 32.0 | 3.2 | 35 | .2 | 4.4 | 69 |
| Second Mesa PM2 | 354749110300101 | 19971211 | .5 | .03 | 134 | .3 | 7.1 | 14.4 |
| Shonto PM2 | 363558110392501 | 19881118 | 45.0 | 6.2 | 5.9 | 1.7 | 13.0 | 14 |

See footnotes at end of table.

**Table 3.** Inorganic and isotope data for the D and N aquifers, Black Mesa area, northeastern Arizona—Continued

| Well or spring name | Site identifier | Date sampled | Fluoride (mg/L) | Silica (mg/L) | Arsenic (μg/L) | Boron (μg/L) | Strontium (μg/L) | Dissolved solids (mg/L) |
|---|---|---|---|---|---|---|---|---|
| Chilchinbito NTUA 1 | 363122110042701 | 19980804 | 0.4 | 8.1 | 1 | 220 | 0.7665 | 1,020 |
| Kitsillie NTUA 1 | 362035110032201 | 19980827 | .7 | 10.3 | 31 | 210 | .2109 | 973 |
| Rough Rock PM5 | 362418109512601 | 19971210 | 1.8 | 13.0 | 48 | 420 | .1370 | 628 |
| 4R-21 | 360826109584001 | 19990812 | .2 | 11.8 | <1 | 230 | 7.5660 | 1,550 |
| 4T-399 | 362150109591801 | 19990811 | .4 | 18.3 | <1 | 100 | 2.7000 | 1,520 |
| 4T-485 | 355548110121801 | 19990811 | 2.7 | 9.79 | --- | 720 | .2580 | 1,110 |
| 6H-12 | 354058110182501 | 19990727 | 4.3 | 8.7 | <1 | 1,140 | .4860 | 1,130 |
| 6H-13 | 353959110203701 | 19990720 | 2.8 | 10.0 | 3 | 940 | .0760 | 719 |
| 6K-304 | 354227110362701 | 19990728 | .9 | 11.3 | 1 | 140 | 1.1700 | 332 |
| 7H-5A-4 | 354122110103901 | 19990722 | 3.3 | 9.3 | <1 | 970 | .0760 | 729 |
| 7H-15 | 354153110072601 | 19990721 | 1.1 | 9.8 | 9 | 330 | .0120 | 330 |
| 7H-52 | 353551110054801 | 19990729 | 1.9 | 6.5 | 2 | 1,040 | .3180 | 1,400 |
| 7K-365 | 354324109581801 | 19990810 | .7 | 12.2 | 2 | 210 | .8400 | 427 |
| 17M-207 | 354030109532801 | 19990810 | .9 | 16.3 | <1 | 380 | 5.0000 | 2,700 |
| Owl Spring | 363504110093701 | 20000404 | --- | --- | --- | --- | --- |  |
| Rough Rock Spring | 362410109521201 | 19960813 | --- | 8.3 | <1 | --- | --- | --- |
| Spider Mound | 354122110054001 | 19990728 | 4.3 | 11.0 | 3 | 1,020 | .0300 | 405 |
| Toyei Academy PM6 | 354214109573801 | 19990813 | .3 | 17.0 | <1 | 80 | 1.3960 | 441 |
| Upper Badger Spring | 360239110515801 | 20000406 | --- | --- | --- | --- | --- | --- |
| Dennehotso PM2 | 365045109504001 | 19971209 | .2 | 12.7 | 6 | 70 | .2576 | 190 |
| Forest Lake NTUA 1 | 361737110180301 | 19980825 | .5 | 18.8 | 3 | 160 | .0466 | 341 |
| Hotevilla PM2 | 355518110400301 | 19971216 | .1 | 25.0 | 3 | 20 | .0132 | 185 |
| Kayenta PM2 | 364344110151201 | 19981201 | 0.2 | 16.6 | 2 | 30 | 0.7578 | 590 |
| Keams Canyon PM2 | 355023110182701 | 19971209 | 1.4 | 13.0 | 42 | 630 | .0519 | 590 |
| Low Mountain PM1 | 355633110064901 | 19960815 | 2.9 | 8.0 | 4 | 1,410 | 2.1544 | --- |
| Moenkopi Spring | 360632111131101 | 19981208 | .2 | 14.1 | 3 | 30 | .4833 | 188 |
| Pasture Canyon Spring | 361021111115901 | 19960815 | .2 | 8.5 | 2 | --- | --- | --- |
| Polacca PM2 | 354848110243401 | 19980828 | .6 | 14.1 | 20 | 240 | .0326 | 318 |
| PWCC 3 | 362625110223701 | 19930128 | .2 | 22.0 | 3 | 30 | .1185 | 169 |
| PWCC 4 | 362647110243501 | 19971210 | .2 | 24.0 | 3 | 20 | .1479 | 139 |
| PWCC 5 | 362901110234101 | 19930128 | .2 | 21.0 | 4 | 40 | .1271 | 112 |
| PWCC 9 | 362333110250001 | 19930128 | .2 | 20.2 | 3 | 30 | .1421 | 94 |
| Red Lake PM1 | 361933110565001 | 19971211 | .2 | 11.0 | <1 | 20 | .5792 | 96 |
| Rocky Ridge PM3 | 360422110353501 | 19981204 | .1 | 21.8 | 3 | 20 | .0106 | 159 |
| Sand Spring | 361011110554401 | 19931013 | .4 | 14.0 | 2 | 560 | 1.3422 | --- |
| Second Mesa PM2 | 354749110300101 | 19971211 | .3 | 21.1 | 15 | 100 | .0206 | 356 |
| Shonto PM2 | 363558110392501 | 19881118 | .1 | 14.0 | --- | 10 | .1804 | 171 |

See footnotes at end of table.

**Table 3.** Inorganic and isotope data for the D and N aquifers, Black Mesa area, northeastern Arizona—Continued

| Well or spring name | Site identifier | Date sampled | $^{87}Sr/^{86}Sr$ | $\delta^{34}S$ (sulfate) (per mil) | $\delta^{18}O$ (sulfate) (per mil) | $\delta^{11}B$ (per mil) | $\delta^{2}H$ (per mil) | $\delta^{18}O$ (per mil) |
|---|---|---|---|---|---|---|---|---|
| Chilchinbito NTUA 1 | 363122110042701 | 19980804 | 0.0708470 | -9.2 | -3.8 | -3.2 | -122.3 | -16.2 |
| Kitsillie NTUA 1 | 362035110032201 | 19980827 | .708490 | -15.2 | -5.9 | -6.4 | -116 | -15.2 |
| Rough Rock PM5 | 362418109512601 | 19971210 | .708290 | -1.1 | 3.3 | 11.6 | -103 | -13.6 |
| 4R-21 | 360826109584001 | 19990812 | .708800 | -1.7 | 9.3 | -6.5 | -78.5 | -11.0 |
| 4T-399 | 362150109591801 | 19990811 | .709710 | 2.0 | 0.9 | 16.7 | -81.6 | -11.4 |
| 4T-485 | 355548110121801 | 19990811 | .708090 | -2.7 | 6.3 | 11.2 | -101.3 | -13.8 |
| 6H-12 | 354058110182501 | 19990727 | .708100 | -7.1 | -.2 | 15.0 | -104 | -13.8 |
| 6H-13 | 353959110203701 | 19990720 | .708180 | .9 | 7.7 | 11.0 | -104 | -13.2 |
| 6K-304 | 354227110362701 | 19990728 | .708330 | 8.8 | 2.2 | 22.0 | -99.4 | -12.5 |
| 7H-5A-4 | 354122110103901 | 19990722 | .708100 | -7.7 | 1.4 | 8.0 | -106 | -14.0 |
| 7H-15 | 354153110072601 | 19990721 | .708220 | 2.5 | 6.6 | 13.7 | -111 | -14.5 |
| 7H-52 | 353551110054801 | 19990729 | .708480 | -11.5 | -3.8 | 2.5 | -109 | -14.1 |
| 7K-365 | 354324109581801 | 19990810 | .708550 | -6.4 | 1.8 | -1.5 | -110.1 | -14.6 |
| 17M-207 | 354030109532801 | 19990810 | .708760 | -2.0 | 5.0 | 13.5 | -83.4 | -11.3 |
| Owl Spring | 363504110093701 | 20000404 | --- | --- | --- | --- | -87.6 | -11.3 |
| Rough Rock Spring | 362410109521201 | 19960813 | .709460 | -2.5 | 2.5 | 18.1 | -99.4 | -11.8 |
| Spider Mound | 354122110054001 | 19990728 | .708240 | 2.7 | 7.8 | 3.2 | -108 | -14.2 |
| Toyei Academy PM6 | 354214109573801 | 19990813 | .708470 | -2.8 | 7.5 | 3.0 | -86.5 | -11.5 |
| Upper Badger Spring | 360239110515801 | 20000406 | --- | --- | --- | --- | -66.7 | -9.0 |
| Dennehotso PM2 | 365045109504001 | 19971209 | .708800 | 1.4 | 3.3 | 7.4 | -82.2 | -10.0 |
| Forest Lake NTUA 1 | 361737110180301 | 19980825 | .709230 | -7.6 | .5 | 5.3 | -106.7 | -13.9 |
| Hotevilla PM2 | 355518110400301 | 19971216 | .708460 | -3.7 | -.6 | 5.6 | -108 | -13.9 |
| Kayenta PM2 | 364344110151201 | 19981201 | .709100 | -14.7 | -2.6 | 13.4 | -82.7 | -10.5 |
| Keams Canyon PM2 | 355023110182701 | 19971209 | .708250 | 8.4 | 6.7 | 3.5 | -101 | -13.4 |
| Low Mountain PM1 | 355633110064901 | 19960815 | .708290 | 10.0 | 11.6 | 17.3 | -106 | -14.2 |
| Moenkopi Spring | 360632111131101 | 19981208 | .709130 | 3.3 | 3.8 | 16.0 | -76.2 | -9.1 |
| Pasture Canyon Spring | 361021111115901 | 19960815 | --- | --- | --- | --- | -77.5 | -8.8 |
| Polacca PM2 | 354848110243401 | 19980828 | .708250 | 7.0 | 2.1 | 3.9 | -102 | -13.4 |
| PWCC 3 | 362625110223701 | 19930128 | .708730 | 4.6 | 2.1 | 4.5 | --- | --- |
| PWCC 4 | 362647110243501 | 19971210 | .709010 | -6.2 | 0.4 | 7.9 | -97.3 | -12.8 |
| PWCC 5 | 362901110234101 | 19930128 | .709040 | -4.6 | 0.3 | 7.0 | --- | --- |
| PWCC 9 | 362333110250001 | 19930128 | .708930 | 5.8 | 0.0 | 1.4 | -101 | -13.5 |
| Red Lake PM1 | 361933110565001 | 19971211 | .708920 | --- | 0.0 | 15.8 | -104 | -13.4 |
| Rocky Ridge PM3 | 360422110353501 | 19981204 | .708250 | -5.9 | -1.7 | 7.4 | -108 | -14.2 |
| Sand Spring | 361011110554401 | 19931013 | .708870 | (2) | (2) | 11.4 | --- | --- |
| Second Mesa PM2 | 354749110300101 | 19971211 | .708230 | 7.5 | -0.4 | -2.4 | -102 | -13.4 |
| Shonto PM2 | 363558110392501 | 19881118 | .709780 | (2) | (2) | 12.6 | -87.6 | -11.0 |

See footnotes at end of table.

**Table 3**. Inorganic and isotope data for the D and N aquifers, Black Mesa area, northeastern Arizona—Continued

| Well or spring name | Site identifier | Date sampled | $^{3}$H (pCi/L) | $\delta^{13}$C (per mil) | $^{14}$C (pmc) | Adjusted $^{14}$C age (years) | $^{14}$C age uncertainty (years) |
|---|---|---|---|---|---|---|---|
| Chilchinbito NTUA 1 | 363122110042701 | 19980804 | <1 | -6.6 | 0.9 | --- | --- |
| Kitsillie NTUA 1 | 362035110032201 | 19980827 | --- | --- | --- | --- | --- |
| Rough Rock PM5 | 362418109512601 | 19971210 | --- | --- | --- | --- | --- |
| 4R-21 | 360826109584001 | 19990812 | <1 | -19.0 | 23.4 | 11,000 | --- |
| 4T-399 | 362150109591801 | 19990811 | <1 | -11.9 | 28.8 | 10,000 | 1,000 |
| 4T-485 | 355548110121801 | 19990811 | <1 | -8.8 | 1.1 | --- | --- |
| 6H-12 | 354058110182501 | 19990727 | <1 | -8.5 | 2.4 | 26,000 | 1,000 |
| 6H-13 | 353959110203701 | 19990720 | 1.0 | -7.2 | 1.4 | 27,000 | 2,000 |
| 6K-304 | 354227110362701 | 19990728 | <1 | -8.9 | 10.4 | 13,000 | 2,000 |
| 7H-5A-4 | 354122110103901 | 19990722 | <1 | -9.1 | 1.1 | 33,000 | 2,000 |
| 7H-15 | 354153110072601 | 19990721 | 2.0 | -8.3 | 5.2 | 20,000 | 1,000 |
| 7H-52 | 353551110054801 | 19990729 | <1 | -10.6 | 4.0 | 21,000 | 4,000 |
| 7K-365 | 354324109581801 | 19990810 | <1 | -10.4 | 12.3 | 15,000 | 2,000 |
| 17M-207 | 354030109532801 | 19990810 | 9.0 | -10.5 | 48.8 | 4,000 | 1,000 |
| Owl Spring | 363504110093701 | 20000404 | 38.0 | --- | --- | --- | --- |
| Rough Rock Spring | 362410109521201 | 19960813 | --- | -10.8 | 92.0 | --- | --- |
| Spider Mound | 354122110054001 | 19990728 | <1 | -8.8 | 1.6 | 28,000 | 2,000 |
| Toyei Academy PM6 | 354214109573801 | 19990813 | <1 | -11.4 | 27.8 | 7,000 | 2,000 |
| Upper Badger Spring | 360239110515801 | 20000406 | 16.0 | --- | --- | --- | --- |
| Dennehotso PM2 | 365045109504001 | 19971209 | --- | --- | --- | --- | --- |
| Forest Lake NTUA 1 | 361737110180301 | 19980825 | <1 | --- | --- | --- | --- |
| Hotevilla PM2 | 355518110400301 | 19971216 | --- | --- | --- | --- | --- |
| Kayenta PM2 | 364344110151201 | 19981201 | --- | --- | --- | --- | --- |
| Keams Canyon PM2 | 355023110182701 | 19971209 | --- | --- | --- | --- | --- |
| Low Mountain PM1 | 355633110064901 | 19960815 | <1 | -12.8 | 1.8 | --- | --- |
| Moenkopi Spring | 360632111131101 | 19981208 | --- | -9.1 | --- | --- | --- |
| Pasture Canyon Spring | 361021111115901 | 19960815 | 29.0 | --- | --- | --- | --- |
| Polacca PM2 | 354848110243401 | 19980828 | --- | -7.5 | 1.2 | --- | --- |
| PWCC 3 | 362625110223701 | 19930128 | --- | --- | --- | --- | --- |
| PWCC 4 | 362647110243501 | 19971210 | --- | --- | --- | --- | --- |
| PWCC 5 | 362901110234101 | 19930128 | --- | --- | --- | --- | --- |
| PWCC 9 | 362333110250001 | 19930128 | <1 | -8.7 | 7.0 | --- | --- |
| Red Lake PM1 | 361933110565001 | 19971211 | --- | --- | --- | --- | --- |
| Rocky Ridge PM3 | 360422110353501 | 19981204 | --- | --- | --- | --- | -- |
| Sand Spring | 361011110554401 | 19931013 | --- | --- | --- | --- | --- |
| Second Mesa PM2 | 354749110300101 | 19971211 | --- | --- | --- | --- | --- |
| Shonto PM2 | 363558110392501 | 19881118 | --- | --- | --- | --- | --- |

See footnotes at end of table.

**Table 3.** Inorganic and isotope data for the D and N aquifers, Black Mesa area, northeastern Arizona—Continued

| Rock formation samples | $^{87}$Sr/$^{86}$Sr | $\delta^{34}$S (sulfate)[3] (per mil) | $\delta^{18}$O (sulfate)[3] (per mil) | $\delta^{13}$C (per mil) |
|---|---|---|---|---|
| Wepo Formation | 0.721728 | 8.5 | -3.2 | -12.8 |
| Toreva Formation | .731744 | 2.5 | 0.0 | -1.3 |
| Mancos Shale | .720766 | 3.3 | 11.8 | -16.2 |
| Dakota Sandstone | .719313 | (2) | (2) | 1.7 |
| Morrison Formation | .712385 | 0.2 | 1.6 | -7.2 |
| Entrada Sandstone | .714423 | (2) | (2) | -2.9 |
| Carmel Formation | .710408 | (2) | (2) | -1.6 |
| Navajo Sandstone | .733010 | (2) | (2) | 1.5 |
| Navajo Sandstone | .717686 | (2) | (2) | --- |
| Navajo Sandstone | .721610 | (2) | (2) | --- |

[1] Unfiltered

[2] Insufficient sulfate in sample for analysis.

[3] Water soluble sulfate in rocks.

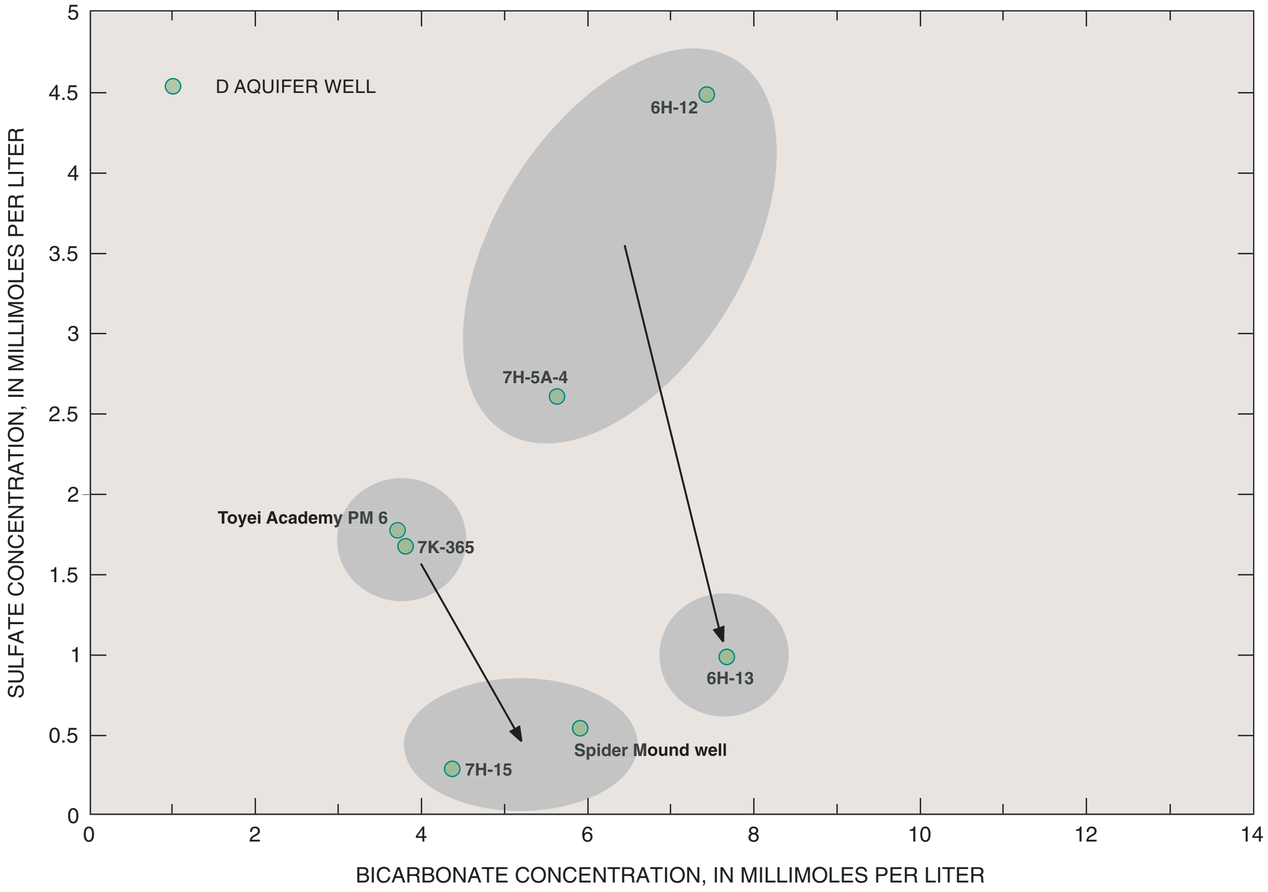


**Figure 7.** Relation between bicarbonate and sulfate concentrations in water from the D aquifer, Black Mesa area, northeastern Arizona.

Ground water in the upgradient parts of the flow path is saturated with respect to calcite, and ground water in the middle part of the flow path is undersaturated with respect to calcite (fig. 8). Equations 3 and 5 show that pH increases as a result of silicate dissolution and sulfate reduction. As pH increases, calcite saturation is exceeded and calcite can precipitate (equation 6):

$$Ca^{2+} + 2HCO_3^{-} = CaCO_3 + H_2O + CO_2. \qquad (6)$$

This process is consistent with the presence of authigenic calcite cement in the aquifer. The decrease in the partial pressure of carbon dioxide ($pCO_2$) from $10^{-1.662}$ to $10^{-3.7533}$ as water moves downgradient further indicates the consumption of acid as silicate hydrolysis proceeds (**fig. 9**). Undersaturation in the middle part of the flow path results from the precipitation of calcite, possibly from the contribution of carbonate into the system through sulfate reduction. Geochemical processes described along the flow paths in the D aquifer are known to require long groundwater residence times.

## ESTIMATED GROUND-WATER AGES FOR THE D AQUIFER

Ground-water age is the amount of time the water has been isolated from the atmosphere and, consequently, represents the amount of time it took to get from the point of entry to the observation point. Ground-water ages (**fig. 10** and **table 3**) in the D aquifer were adjusted using NETPATH (Plummer and others, 1994). The model by Fontes and Garnier (1979) was used to account for the dilution of the carbon during water-rock interactions through isotopic exchange.

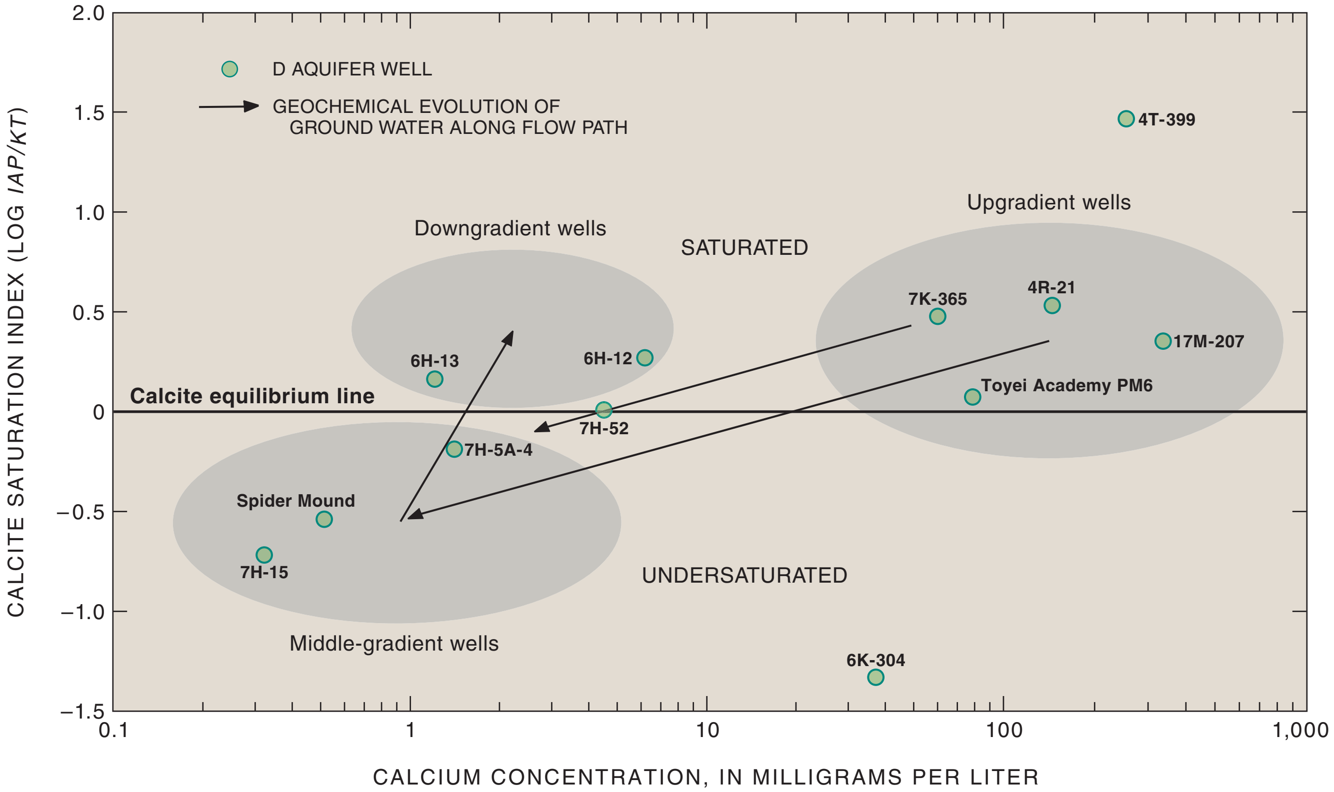


**Figure 8.** Relation between calcium concentrations and calcite saturation indices in water from the D aquifer, Black Mesa area, northeastern Arizona.

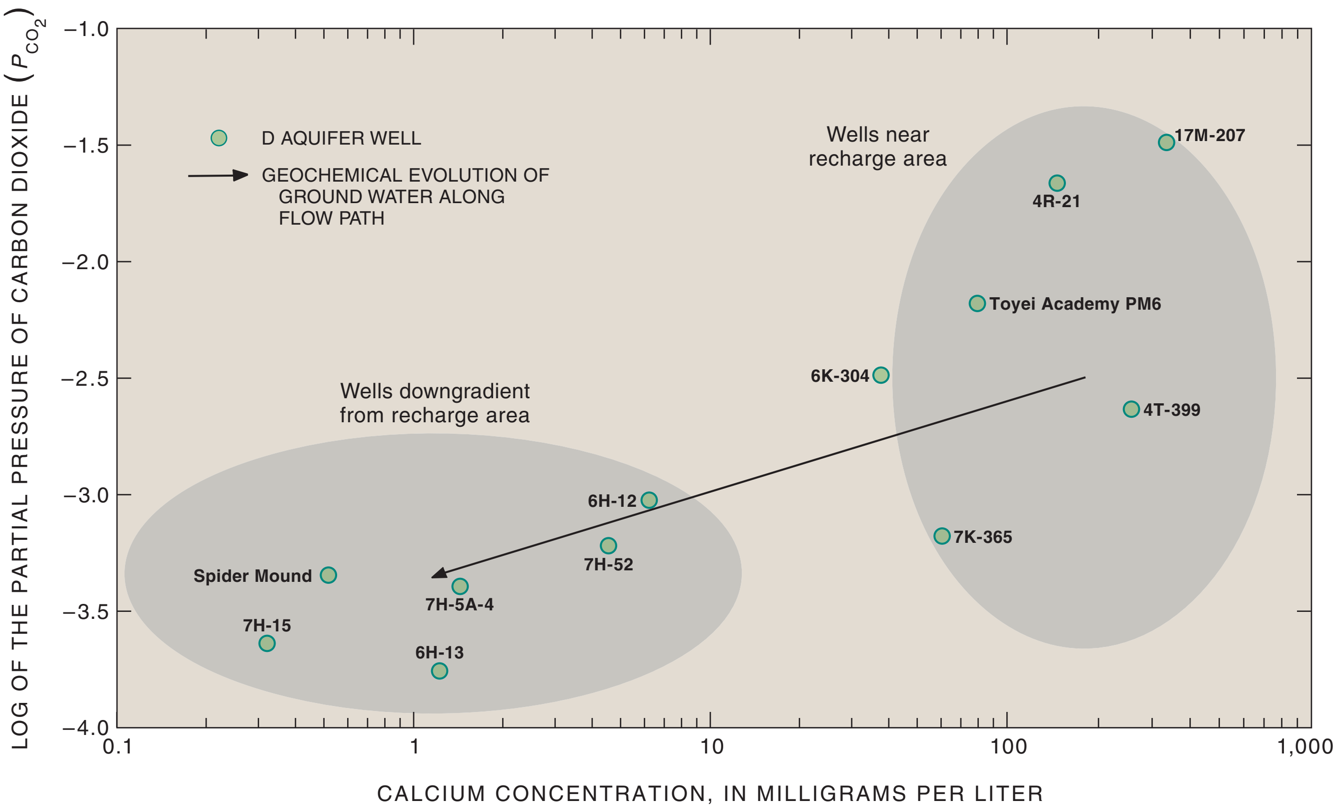


**Figure 9.** Relation between calcium concentrations and the log of the partial pressure of carbon dioxide in water from the D aquifer, Black Mesa area, northeastern Arizona.

An estimated soil-gas $\delta^{13}C$ value of -17 ‰ was used consistently for each site. This value was obtained by varying the value of soil-gas $\delta^{13}C$ used as input to the model from -12 ‰ to -20 ‰ and comparing the $\delta^{13}C$ value computed for ground water at each well to the measured value. The range of soil-gas values used is considered typical for C4[1] plants in the Southwest (L. Neil Plummer, hydrologist, U.S. Geological Survey, oral commun., 1996). A soil-gas $\delta^{13}C$ value of -17 ‰ produced computed $\delta^{13}C$ values that were consistently comparable with measured values. Adjusted ground-water ages from the Fontes and Garnier model calculations were 4,000 to 11,000 years near the recharge area (well 17M-207), 33,000 years near the middle of the flow path (well 7H-5A-4), and 13,000 years near the end of the flow path (well 6K-304; fig. 10 and table 3). Springs sampled during this study yielded modern ground water.

An analysis was done to determine the sensitivity of adjusted ground-water ages to measured $\delta^{13}C$ values from rock units and estimated soil-gas $\delta^{13}C$ values.

Results from Spider Mound well are presented in table 4 to demonstrate the sensitivity of adjusted ages to both the $\delta^{13}C$ values from rock units and the estimated soil-gas $\delta^{13}C$ values. The sensitivity analysis for Spider Mound well yielded average adjusted ground-water ages that ranged from 25,000 years to 39,000 years when both the soil-gas $\delta^{13}C$ values and the $\delta^{13}C$ values from rock units were allowed to vary; however, uncertainties of ± 2,000 to 3,000 years were consistent within a given range of soil-gas $\delta^{13}C$ values (table 3). A sensitivity analysis for only the measured $\delta^{13}C$ values from rock units was done for all other D aquifer wells because -17 ‰ was consistently used to adjust for carbon ages (table 3).

---

[1] Three photosynthetic pathways exist among terrestrial plants: $C_3$, $C_4$, and CAM (crassulacean acid metabolism) photosynthesis. $C_4$ plants include warm season grasses and a few shrubs (Kendall and McDonnell, 1998, p. 578).

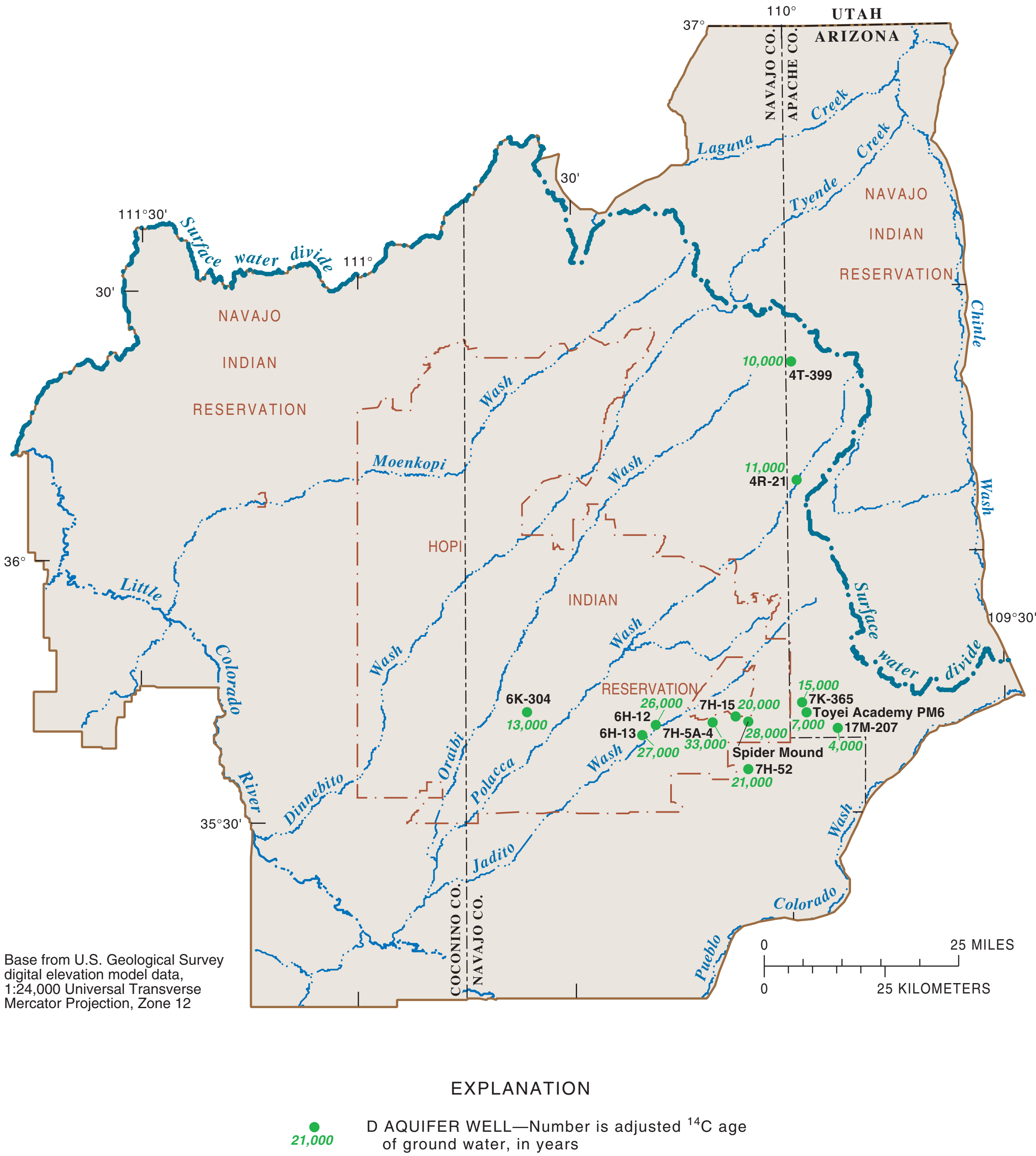


**Figure 10**. Adjusted $^{14}$C ages of ground water in the D aquifer, Black Mesa area, northeastern Arizona.

**Table 4.** Sensitivity analysis of $^{14}C$ ages for water from Spider Mound well, Black Mesa area, northeastern Arizona

[$A_o$, initial $^{14}C$ activity at Spider Mound well, in percent modern carbon; OA, overadjusted]

| Measured $\delta^{13}C$ value for specified formation (per mil) | Ingerson and Pearson (1964) | | Fontes and Garnier (1979) | | Eichinger (1983) | |
|---|---|---|---|---|---|---|
| | $A_o$ | $^{14}C$ adjusted age (years) | $A_o$ | $^{14}C$ adjusted age (years) | $A_o$ | $^{14}C$ adjusted age (years) |
| **Initial $\delta^{13}C$ in soil gas at -12 per mil** | | | | | | |
| (Carmel) -1.61 | 69.49 | 31,072 | 150.35 OA | OA | 64.85 | 30,501 |
| (Dakota) +1.67 | 76.81 | 31,900 | 119.81 OA | OA | 73.54 | 31,540 |
| (Entrada) -2.87 | 65.28 | 30,556 | 230.55 OA | OA | 59.78 | 29,828 |
| **Initial $\delta^{13}C$ in soil gas at -15 per mil** | | | | | | |
| (Carmel) -1.61 | 53.53 | 28,975 | 60.32 | 29,903 | 49.87 | 28,330 |
| (Dakota) +1.67 | 62.99 | 30,260 | 76.3 | 31,845 | 59.98 | 29,856 |
| (Entrada) -2.87 | 49.13 | 38,307 | 49.07 | 28,196 | 44.49 | 27,386 |
| **Initial $\delta^{13}C$ in soil gas at -20 per mil** | | | | | | |
| (Carmel) -1.61 | 39.26 | 26,352 | 38.81 | 26,256 | 36.01 | 25,638 |
| (Dakota) +1.67 | 48.46 | 28,092 | 48.39 | 28,081 | 45.88 | 27,640 |
| (Entrada) -2.87 | 34.79 | 25,354 | 34.1 | 25,189 | 31.19 | 24,451 |

| Site name | Measured $\delta^{13}C$ value (per mil) | $\delta^{13}C$ soil gas (per mil) | $^{14}C$ corrected age (years) | $A_o$ | Solid phase |
|---|---|---|---|---|---|
| Spider Mound | -1.61 | -17 | 28,000 | 46.75 | Carmel Formation |
| Spider Mound | 1.67 | -17 | 30,000 | 61.34 | Dakota Sandstone |
| Spider Mound | -2.87 | -17 | 27,000 | 41.75 | Entrada Sandstone |

The ground-water ages generally increase in the downgradient direction; however, younger adjusted ground-water ages along the flow path (fig. 10) suggest a component of younger local recharge to the system. The local recharge water contains $^{14}C$ that is younger than the $^{14}C$ in the existing ground water, and the combination of waters results in younger ages of ground-water samples. Although ground-water samples from discrete zones within an aquifer are preferred for most ground-water studies, samples from many of the wells in this study consisted of water derived from multiple water-bearing zones through large intervals of perforated casing or open borehole. Pumping of wells during sample collection induced mixing of water from the different zones. Measurable amounts of $^{3}H$ in samples from wells 6H-13, 7H-15, and 17M-207 (**table 3**) indicate younger ground-water ages resulting from local recharge. The younger ages at well 6K-304 and 6H-12 (**fig. 10**) determined from the $^{14}C$ data indicate a component of younger water at these sites also; however, no measurable amounts of $^{3}H$ were detected in the samples. The Mancos Shale is absent at these wells, so direct local recharge could occur in this area. NETPATH was used to back calculate a soil-gas $\delta^{13}C$ value for an open system to test the hypothesis that the unconfined conditions of the D aquifer at well 6K-304 do not affect the estimated soil-gas $\delta^{13}C$ input value. NETPATH calculated a $\delta^{13}C$ value of -17.3 ‰, which is nearly the same as the value of -17 ‰ used as input in all the models.

Ground-water ages in the D aquifer are similar to those in the N aquifer reported by Lopes and Hoffmann (1997). Because ground-water ages in both aquifers increase in the downgradient direction and the ages are about 20,000 years in the area of apparent leakage, it is possible that the leakage occurs naturally as a result of differences in head between the two aquifers. The similarity in ages for the D and N aquifers suggest that the ground-water systems were recharged during a similar recharge regime.

## RECHARGE TO THE D AQUIFER

In most of the Black Mesa area, the Mancos Shale overlies the D aquifer and impedes downward movement of water. Recharge to the aquifer through unconsolidated material in the eastern area of Black Mesa, and where the Dakota Sandstone, Morrison Formation, and Entrada Sandstone crop out, has been estimated at 5,392 acre-ft/yr (HSI GeoTrans, Inc. and Waterstone Environmental Hydrology and Engineering, Inc., 1999).

To provide insight to recharge locations, D aquifer wells were sampled to obtain $\delta^{18}O$ and $\delta^{2}H$ data. These data were plotted together with data from N aquifer samples (**fig. 11**). The tight clustering of data from the two aquifers is evidence that ground water in the D aquifer recharged under the same climatological conditions as water in the N aquifer. Lopes and Hoffmann (1997) concluded that about 94 percent of ground water in the N aquifer was recharged during the last Pleistocene glacial age when the climate was colder and more humid than at present, conditions during which recharging waters would have been more depleted in $^{2}H$ (Merlivat and Jouzel, 1979). The equation for the modern-day slope of the meteoric water line (Craig, 1961a) is:

$$\delta^{2}H = 8\delta^{18}O + 10, \qquad (7)$$

and the equation for the local Pleistocene meteoric water line estimated by Lopes and Hoffmann (1997) is:

$$\delta^{2}H = 8\delta^{18}O + 4. \qquad (8)$$

Paleoclimatic effects on isotopic compositions can be identified along the ground-water flow path in the D aquifer. Depletion by 2.9 ‰ in $\delta^{18}O$ between younger water at the upgradient wells and older water at the downgradient wells indicates that the downgradient water recharged during a significantly cooler climate (fig. 11). N aquifer water showed an average shift of 3.3 ‰ in $\delta^{18}O$ from the unconfined part of the aquifer in the recharge area to the older confined part of the aquifer (Lopes and Hoffmann, 1997). Lopes and Hoffmann reported that this shift corresponds to a 5.9° C rise in temperature since the last glacial period. The heavier isotopic compositions of waters near the recharge areas in the D aquifer reflect this gradual climatic warming.

The $\delta^{18}O$ shift along the ground-water flow path indicates that there is no recharge occurring near wells in the middle part of the flow path where the adjusted $^{14}C$ ages range from 21,000 to 33,000 years. Varying amounts of recharge may be occurring locally near wells that yield slightly younger water (4,000 to 21,000 years). Driller's logs for Spider Mound, 7K-365, 7H-15, and 7H-52 indicate that the Mancos Shale underlies unconsolidated surficial deposits in most of the southeastern part of Black Mesa. Driller's logs for 17M-207, Toyei Academy PM6, and 4R-21 indicate that the Dakota Sandstone and (or) the Morrison Formation underlie unconsolidated surficial deposits, or the Bidahochi Formation where it crops out, and enable direct recharge from infiltration. $^{3}H$ data from well 17M-207 (9 pCi/L; table 3) indicate that the D aquifer is receiving some recharge in this area.

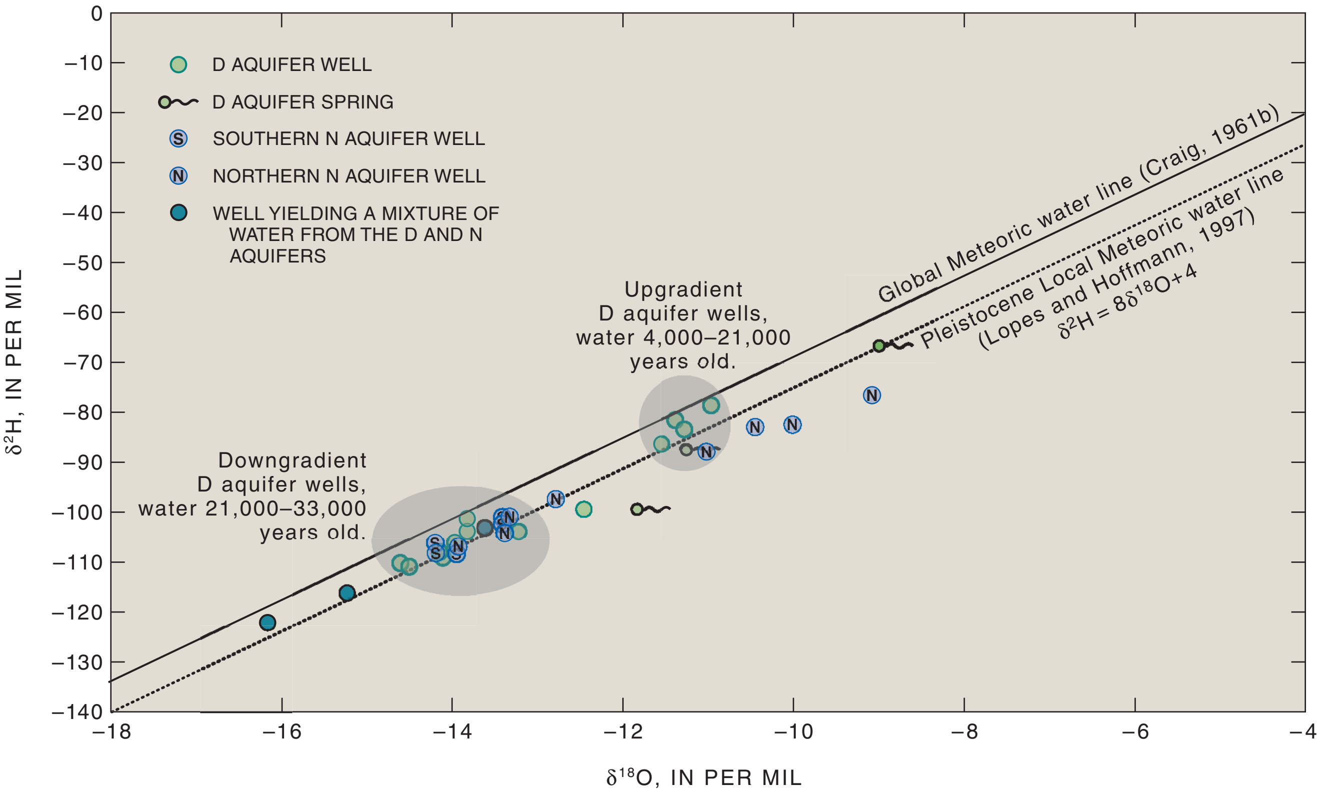


**Figure 11.** Relation between $\delta^{18}O$ and $\delta^2H$ values in water from the D and N aquifers, Black Mesa area, northeastern Arizona.

## GROUND-WATER LEAKAGE FROM THE D AQUIFER TO THE N AQUIFER

Leakage from the D aquifer to the N aquifer has been occurring in the Black Mesa Basin for thousands of years. Geochemical and isotopic evidence of leakage is evident where the N aquifer is thin and the predevelopment hydraulic gradient and lateral flow rates are small. $^{87}Sr/^{86}Sr$ data from ground-water samples are an indicator for areas where leakage is occurring and not being diluted. Evidence for increased leakage from ground-water development in the last few decades may not be detectable.

Wells developed into the confined part of the N aquifer in the northern area of Black Mesa sampled for this study (PWCC 9, PWCC 5, PWCC 4, PWCC 3, and Forest Lake NTUA 1) are in an area where the hydraulic gradient in the N aquifer is large. Any geochemical evidence of leakage from the D aquifer may be diluted. Wells developed into the confined part of the N aquifer in the southern part of Black Mesa (Low Mountain PM1, Keams Canyon PM2, Second Mesa PM2, Polacca PM2, Hotevilla PM2, and Rocky Ridge PM3) are in an area where the predevelopment hydraulic gradient is small and geochemical evidence of leakage will not be diluted. Lopes and Hoffmann (1997) provided geochemical evidence for leakage in the southern areas of Black Mesa where leakage has been occurring over a long period of time. Marley and others (1999) suggested that the apparent mixing of water between the two aquifers in the southeastern area can be explained in part by faulty well construction; however, the heterogeneity of the Carmel Formation and the differences in water levels between the two aquifers are such that leakage through the Carmel can be expected to occur under natural conditions in parts of the study area (Harshbarger and others, 1957; Cooley and others, 1969; Eychaner, 1983). $^{87}Sr/^{86}Sr$ data provide evidence of leakage in the southern areas of Black Mesa.

$^{87}Sr/^{86}Sr$ values from the N aquifer are expected to be larger than values from the D aquifer because rock units of the N aquifer are older than those of the D aquifer. $^{87}Sr/^{86}Sr$ values from N aquifer wells in the northern area of Black Mesa were larger than values from D aquifer wells; however, values from N aquifer wells in the southern area of Black Mesa were similar to values from D aquifer wells (**fig. 12** and **table 3**). Wells developed into the N aquifer that enable mixing of water from the two aquifers because of faulty well construction (Greg Littin, U.S. Geological Survey, oral commun., 1999; Chilchinbito NTUA 1, Kitsillie NTUA 1, and Rough Rock PM 5) yielded $^{87}Sr/^{86}Sr$ values that are nearly the same as values from D aquifer wells.

Statistical analysis revealed a significant difference in $^{87}Sr/^{86}Sr$ values between ground water from the N aquifer in the northern areas of Black Mesa and ground water from the N aquifer in the southern area of Black Mesa and between ground water from the N aquifer in the northern area of Black Mesa and ground water from the D aquifer (**fig. 13**). No statistically significant differences were noted between ground water from the D aquifer and ground water from the N aquifer in the southern area of Black Mesa. The geographical distribution of $^{87}Sr/^{86}Sr$ values in the Black Mesa area indicate that leakage is occurring in areas far from the recharge area where the N aquifer is thin and the lateral-flow component is small (**fig. 14**). Lopes and Hoffmann (1997) suggested that boron or sulfate concentrations could be used to delineate the leakage boundary. $\delta^{34}S_{(sulfate)}$ and $\delta^{11}B$ values from ground water in the D and N aquifers in this study, however, are not significantly different (fig. 13) and do not provide discernible evidence for leakage.

Ground-water monitoring of the N aquifer has shown that vertical drawdowns have increased the differences between the potentiometric surfaces of the D and N aquifers by greater than one-third in the area of most apparent leakage (Thomas, 2002, fig. 5). Water levels measured in six D aquifer wells for this study indicated that there has not been significant drawdowns since the wells were first developed in the 1950s. Water-level declines near Low Mountain and Keams Canyon would be expected to increase vertical leakage from the D aquifer and increase horizontal flow in the N aquifer. Potential increases in leakage from the D to the N aquifer would change the mixing ratio and, therefore, could result in a shift of water chemistry toward either the water chemistry of the D aquifer or the water chemistry of the N aquifer. The USGS Black Mesa monitoring program has not detected any significant changes in the major-ion water chemistry of the N aquifer that are related to induced leakage (Thomas, 2002). The system, however, has evolved to the present conditions over thousands of years, and although development has caused an increase in the hydraulic gradient over the past few decades, geochemical evidence may take centuries to be detectable. A more quantitative answer to the these changes will require additional information on the Carmel Formation and simulation modeling.

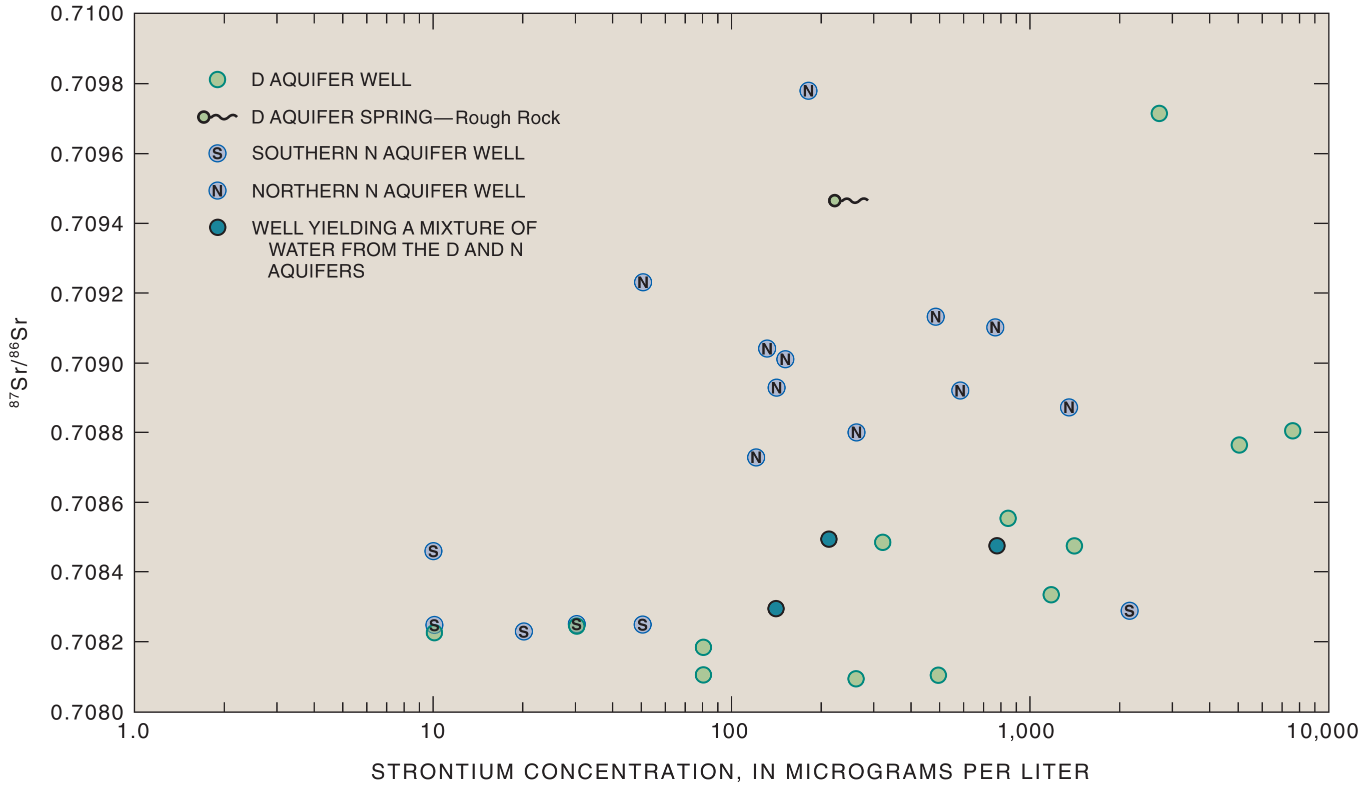


**Figure 12**. Relation between strontium concentrations and $^{87}Sr/^{86}Sr$ values in water from the D and N aquifers, Black Mesa area, northeastern Arizona.

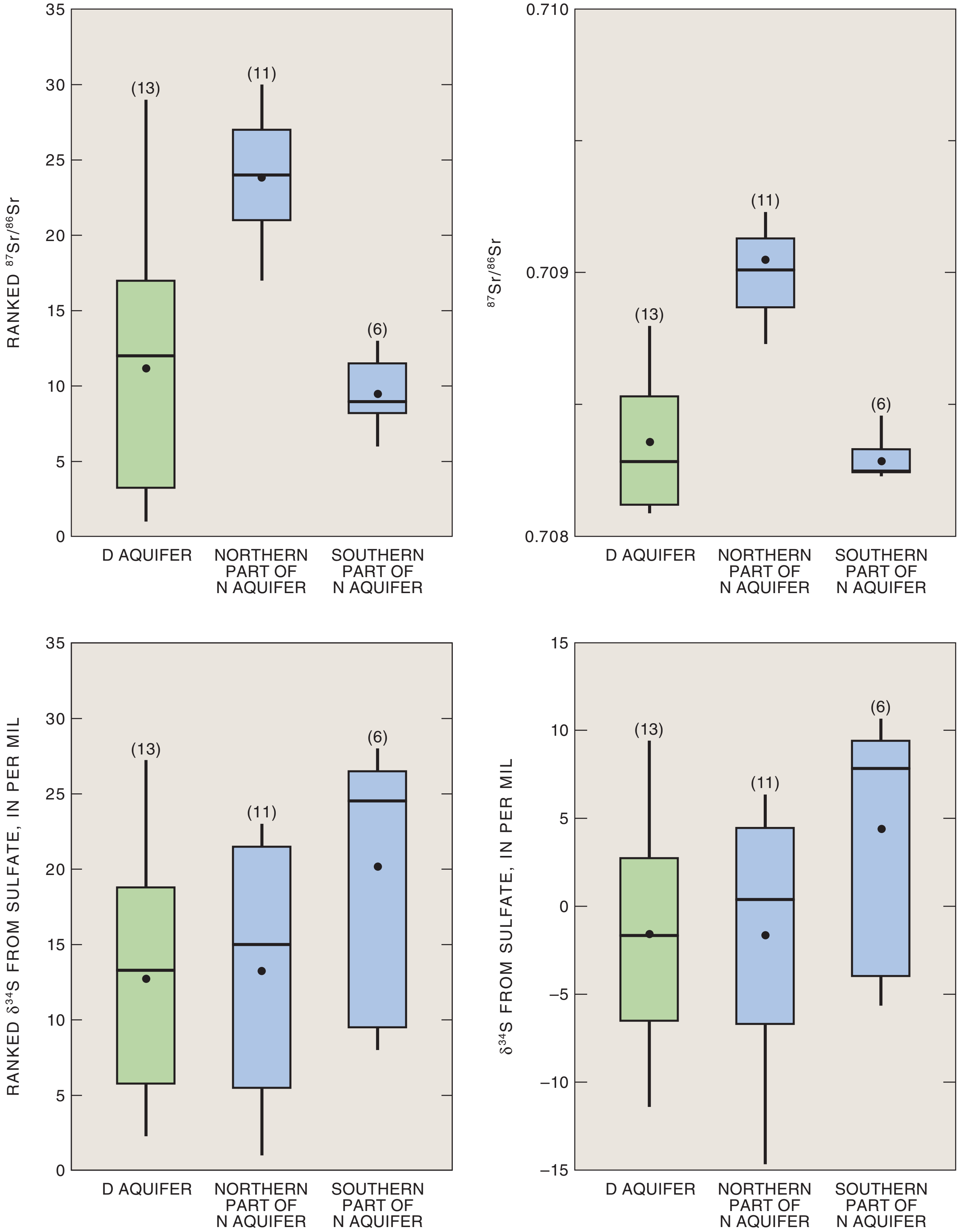


**Figure 13**. Isotopic data for $^{87}Sr$, $^{34}S$ from sulfate, and $^{11}B$ in water from the D and N aquifers, Black Mesa area, northeastern Arizona.

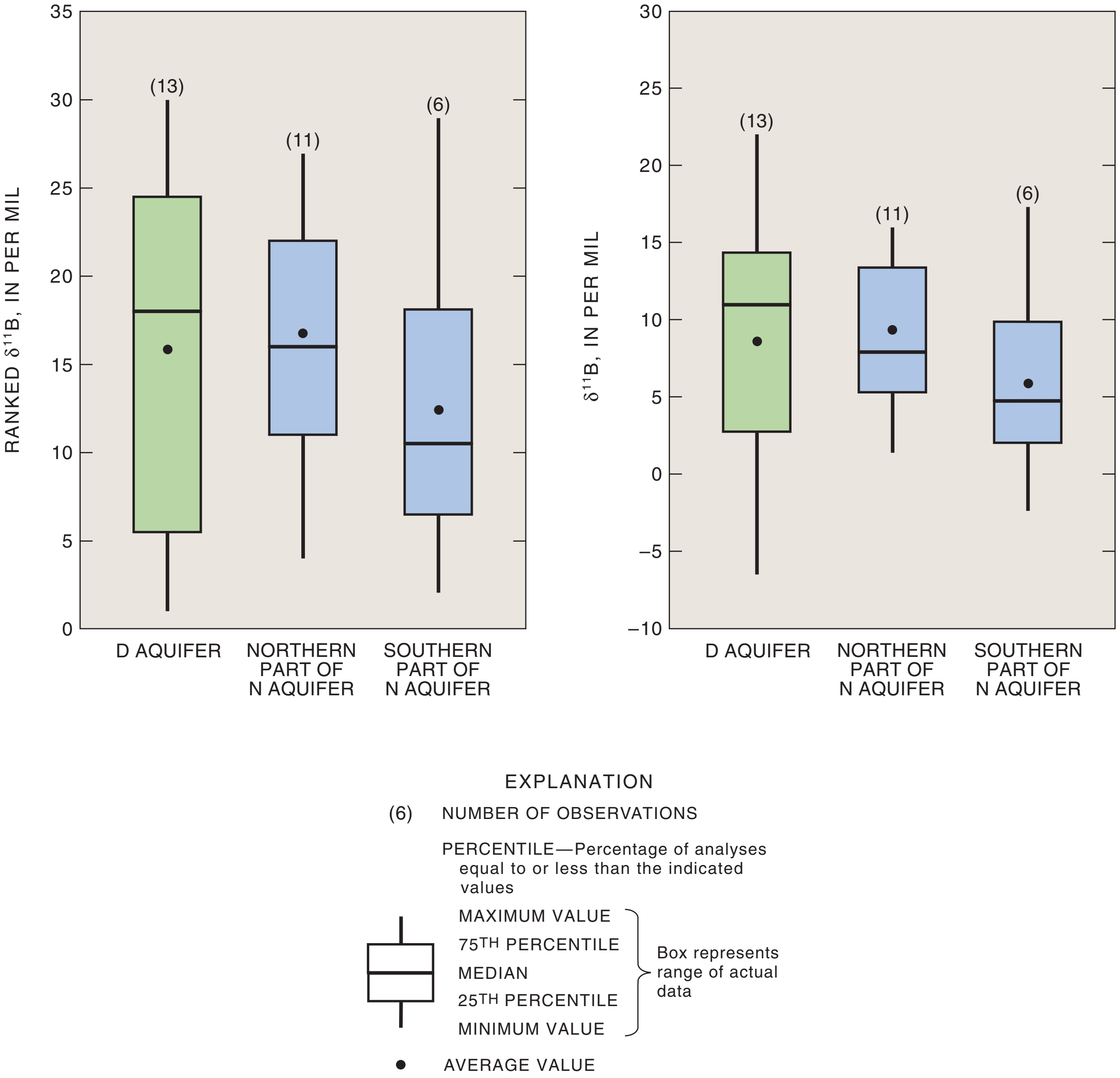


**Figure 13**. Continued.

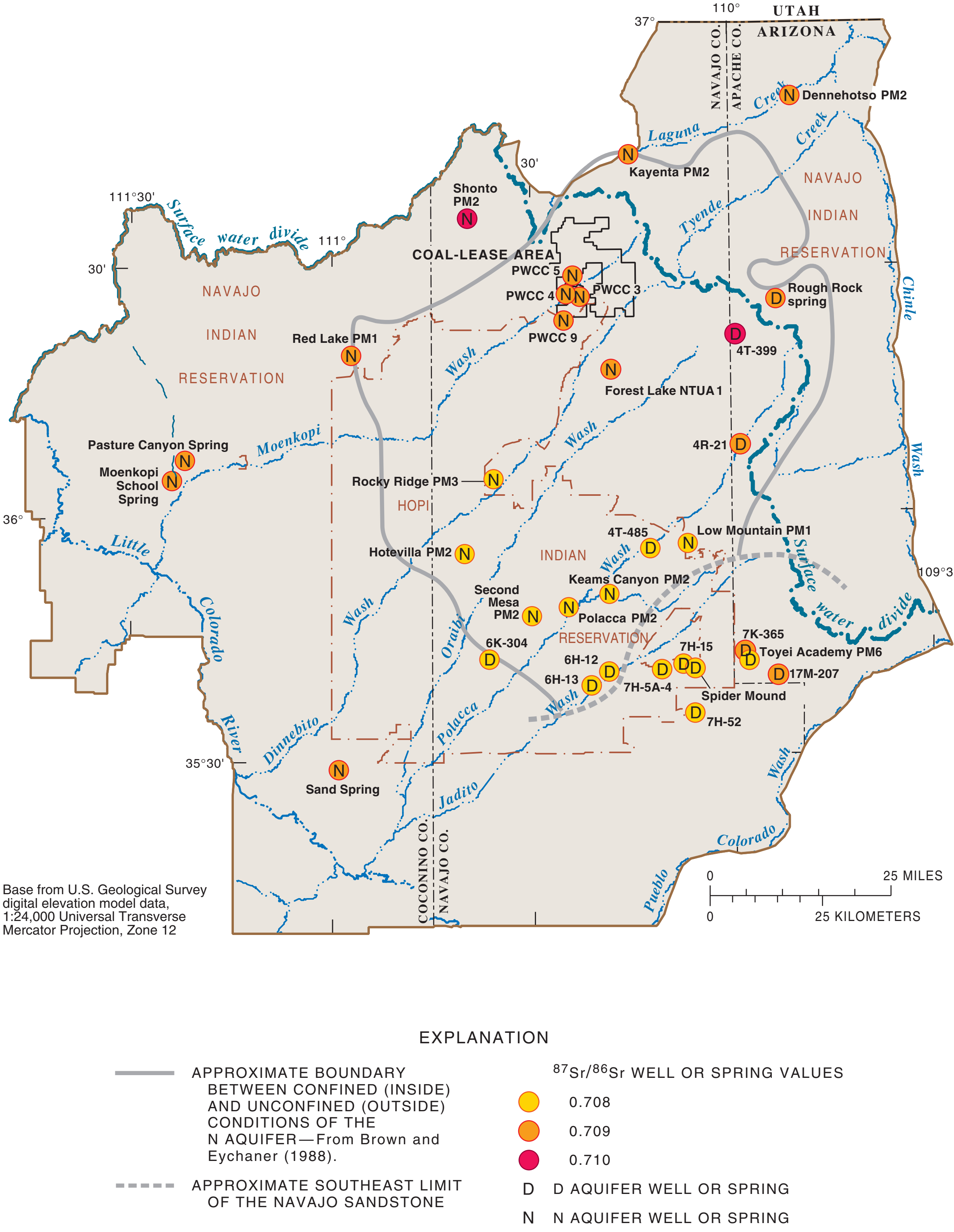


**Figure 14.** $^{87}Sr/^{86}Sr$ values in ground water at wells in the Black Mesa area, northeastern Arizona.

## SUMMARY AND CONCLUSIONS

The Black Mesa area in northeastern Arizona is an arid region within which the Navajo Nation and Hopi Tribe depend on ground water for municipal and livestock purposes. Withdrawl of ground water in the Black Mesa area is primarily from the D and N aquifers. The D aquifer is composed of sandstones, mudstones, shales, and clays. Water quality in the D aquifer is varied because of the mineralogic heterogeneity of the hydrogeologic units. The Mancos Shale is thick and fine grained, overlies much of the D aquifer, and prevents percolating water from reaching the aquifer. Withdrawals from the D aquifer are typically for livestock purposes. The N aquifer is a homogeneous clean quartz sandstone and is the primary source of water for domestic use by the Navajo Nation and Hopi Tribe. Increased pumpage from the N aquifer has raised concerns about induced leakage from the overlying D aquifer, which would deleteriously affect the water quality of the N aquifer. Chemical data were used as an independent means of characterizing the D aquifer, improving the understanding of similarities and differences between the D and N aquifers, and identifying areas of leakage.

The dissolution of alkali feldspar contributes the initial source of dissolved sodium in the D aquifer ground water. Cation exchange is contributing to the higher sodium concentrations in some parts of the flow path. Sulfate concentrations reflect contributions of sulfur from the dissolution of gypsum and ground-water interaction with lignite seams. $\delta^{34}S_{(sulfate)}$ values indicate that sulfur reduction is occurring in areas downgradient of where ground water is in contact with lignite seams and a source of organic carbon is available for microbial reduction. Hydrolysis of feldspar and sulfate reduction both contribute bicarbonate to the system that augments the precipitation of calcite once initial ground waters become oversaturated.

Adjusted ground-water ages for the D aquifer are 4,000 to 11,000 years near the recharge area, 33,000 years in the middle part of the flow path, and 13,000 years in the downgradient area. Detectable amounts of $^3H$ in water from a few wells imply mixing is occurring between older, deeper ground water and younger, shallower ground water in some areas. Ground-water ages and $\delta^{18}O$ and $\delta^2H$ values suggest that most of the water in the D aquifer was recharged more than 10,000 years ago when the climate was cooler and more humid than at present. The similarity of ground-water ages in the D aquifer to ages in the N aquifer suggests that leakage has been occurring for thousands of years.

Leakage is most likely to occur in the southern part of Black Mesa, far from the recharge area of the N aquifer and where the prestress hydraulic gradient is small. The differences between the potentiometric surface of the D aquifer and the prestress potentiometric surface of the N aquifer in the southern areas of Black Mesa are small. Ground-water monitoring on Black Mesa has shown that vertical-head differences between the D and N aquifers have increased by more than one-third. $^{87}Sr/^{86}Sr$ values for water from the D and N aquifers delineated areas where leakage is occurring. N aquifer wells in the northern part of Black Mesa yielded water with larger $^{87}Sr/^{86}Sr$ values than water from D aquifer wells. N aquifer wells in the southern areas of Black Mesa yielded water with $^{87}Sr/^{86}Sr$ values similar to values measured in the D aquifer. Ground-water development during the last few decades could have increased the hydraulic gradient in the N aquifer, resulting in a dilution of any geochemical changes caused by induced leakage.

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