



Geochemistry of Major Aquifers and Springs

By Laurie Wirt and Ed DeWitt

Chapter E

Geologic Framework of Aquifer Units and Ground-Water Flowpaths, Verde River Headwaters, North-Central Arizona

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Geochemistry of Major Aquifers and Springs

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Abstract

In this chapter, graphical methods to plot geochemical and isotopic data are used to characterize major aquifers and springs discharging to the upper Verde River and to identify changes in water chemistry along the main ground-water flowpath from Big Chino Valley to upper Verde River springs. Samples were analyzed for major and trace elements, $\delta^{18}\text{O}$, δD , ^3H , ^{14}C , and ^{13}C . Ground-water samples are grouped by aquifer, altitude, and geographic location to identify important processes and trends. Sample groups include (a) high-altitude areas west and south of Big Chino Valley, (b) the carbonate aquifer north of Big Chino Valley and the upper Verde River (Mississippian-Devonian, or M-D sequence), (c) the Little Chino basin-fill aquifer, (d) the Big Chino basin-fill aquifer, (e) the carbonate aquifer near the outlet of the Big Chino basin-fill aquifer (Devonian-Cambrian, or D-C zone), and (f) low-altitude springs discharging to the upper Verde River.

Limitations of the stable-isotope data used in this study include not being able to volumetrically weight contributions from different areas of the ground-water system. Also, evaporation has had a significant effect on the stable-isotope composition of spring-fed lakes and some samples from the M-D carbonate aquifer. Despite these drawbacks, the Little Chino basin-fill aquifer and the M-D sequence still could be largely excluded as major sources to upper Verde River springs. Low-altitude springs discharging from the Little Chino basin-fill aquifer are ~ 0.4 per mil (‰) enriched in $\delta^{18}\text{O}$, with high dissolved strontium ($> 450 \mu\text{g/L Sr}$) resulting from contact latite-andesite in northern Little Chino Valley. In contrast, the M-D sequence is depleted by about 1.3‰ $\delta^{18}\text{O}$ and 7.9‰ δD and is low in strontium (less than $120 \mu\text{g/L Sr}$), compared to moderate values for upper Verde River springs (346 to $440 \mu\text{g/L Sr}$).

Water chemistry of upper Verde River springs has characteristics of both the Big Chino basin-fill aquifer and the D-C zone of the carbonate aquifer near Paulden. Values of $-10.3 \pm 0.2\text{‰}$ $\delta^{18}\text{O}$ and $-74.4 \pm 2.0\text{‰}$ δD were used to trace a flowpath from the Big Chino basin-fill aquifer near Paulden through the D-C zone to upper Verde River springs. Disproportionate increases of the boron and lithium along the flowpath of 274 percent B versus 188 percent Li (with no corresponding change in $\delta^{18}\text{O}$, δD , Ca, and Sr values) indicate the major process responsible for increases in trace elements is water-rock interaction. The upper Verde River springs samples

have moderately high values of $17\text{--}29 \mu\text{g/L As}$, $136\text{--}270 \mu\text{g/L B}$, and $28\text{--}49 \mu\text{g/L Li}$, attributed to water-rock contact with marine shale within the D-C zone. The highest concentrations in the study area of $33\text{--}38 \mu\text{g/L As}$, $330\text{--}460 \mu\text{g/L B}$, and $54\text{--}86 \mu\text{g/L Li}$ are found in the D-C zone.

The presence of measurable tritium and elevated ^{14}C activity near the outlets of the basins indicates that recharge is occurring beneath major drainages, including Williamson Valley Wash, lower Big Chino Wash, Granite Creek, and Little Chino Creek. Carbon-14 activities along the flowpath between the Big Chino basin-fill aquifer near Paulden area and upper Verde River springs range between 55 and 42 percent modern carbon, compared with 18 percent modern carbon for a well in the D-C zone north of Paulden. Along the final leg of the flowpath to upper Verde River springs, the ^{14}C activity decreases slightly from 55.5 ± 0.6 to 42 ± 0.3 percent modern carbon, which is attributed either to water-rock interaction or a small amount of mixing.

No mixing of the Big Chino basin-fill aquifer with a second source is needed to account for the stable-isotope composition and trace-element chemistry at upper Verde River springs. Despite the lack of compelling geochemical evidence to support mixing between the carbonate aquifer and the Big Chino basin-fill aquifer, however, a standard analytical uncertainty of $0.2 \delta^{18}\text{O}\text{‰}$ would allow approximately 15 percent of the total discharge to upper Verde River springs to be derived from the M-D sequence of the carbonate aquifer. Multiple lines of geochemical evidence are consistent with a basin outlet flowpath from the Big Chino aquifer near Paulden through the D-C zone of the carbonate aquifer to upper Verde River springs.

Introduction

The goal of the geochemical and isotopic studies in this chapter is to identify ground-water flowpaths and source(s) of springs discharging to the upper Verde River. From 2000 to 2004, water-chemistry samples were collected from the Big and Little Chino basin-fill aquifers, from high-altitude springs and tributaries of the Bradshaw, Santa Maria, and Juniper Mountains, and from the carbonate aquifer north of Big Chino Valley and the upper Verde River (fig. E1). A variety of geochemical methods were used to infer recharge sources, define ground-water flowpaths, and to show differences in the

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apparent ages of ground water contributing to the upper Verde River. Geochemical and stable isotope results of past studies also were utilized when appropriate.

Geochemical approaches used in this study include major- and trace-element concentrations, stable (or nonradioactive) isotopes of oxygen, hydrogen, and carbon, and radioactive tritium and carbon-14. Concentrations of major ions and trace elements help to define processes related to water-rock interactions and possible mixing of end members. Stable isotopes of oxygen and deuterium provide information about the altitude of ground-water recharge areas and the degree of evaporation. Tritium and carbon-14 are used to identify changes in the apparent age of ground water along major flowpaths. Hydrologic and geologic information developed in the conceptual hydrogeologic framework (Chapter D, this volume) was utilized in sampling strategy and helped to constrain ground-water flow directions, evaluate spatial differences in solutes and environmental isotopes, and infer probable sources of dissolved species. Geochemical trends are particularly useful for delineating flowpaths through fractured rock aquifers and for evaluating whether concentrations of certain elements are caused by water-rock interactions or by ground-water mixing.

Purpose and Scope

The purpose of this chapter is to identify geochemical trends for the Big and Little Chino basin-fill aquifers, the regional carbonate aquifer, and for springs discharging to the upper Verde River. Geochemical and isotope methods are used (1) to characterize the water chemistry of major aquifers, recharge areas, and springs in the upper Verde River, (2) to identify water-rock interactions along flowpaths through fractured rock near the outlets of Big and Little Chino Valleys, (3) to delineate areas where recharge is occurring, and (4) to determine whether ground water discharging to upper Verde River springs is derived from a single source (e.g. the Big Chino basin-fill aquifer) or is comprised of a mixture of ground water from the Big Chino aquifer with the adjacent carbonate aquifer.

Previous Investigations

Previous hydrological investigations of the headwaters have used concentrations of major elements to describe water quality. In 1946 and 1947, H.B. Babcock of the U.S. Geological Survey (USGS) collected what are perhaps the earliest water-quality analyses for wells in Little Chino Valley (Krieger, 1965; table 18). Several other studies have plotted chemical parameters on maps to compare and to characterize similar and dissimilar types of water. In Big Chino Valley, Wallace and Laney (1976) plotted specific conductivity, and Schwab (1995) plotted chemical-quality diagrams of major cations and anions. Remick (1983) mapped total-dissolved solids for Big and Little Chino Valleys. These studies surmise

that ground water in the headwaters region generally is of excellent quality and suitable for most uses, except for the occurrence of moderate to high amounts of dissolved arsenic in samples from the southeastern end of Big Chino Valley (Schwab, 1995).

Several studies have used water chemistry and stable-isotope analyses to characterize ground water in the headwaters. In 1986–87, the USGS collected six ground-water samples in Big and Little Chino Valleys as part of a regional aquifer-system analysis of basins in the southwestern United States (Robertson, 1991). In the summer of 1991, the USGS collected stream samples and conducted a seepage study of base flow in the upper Verde River. Twelve samples also were collected from wells and springs in Big and Little Chino basins in cooperation with Arizona Department of Water Resources. The joint effort was part of a hydrologic and geologic study by the Bureau of Reclamation to investigate the Big Chino aquifer as a possible source of water for the city of Prescott (Ewing and others, 1994).

Past stable-isotope interpretations have been a basis for conflicting conclusions about the source of upper Verde River springs. Arizona State University (ASU) conducted a 2-year stable-isotope (^2H and ^{18}O) investigation of ground and surface-water in the Verde River headwaters (Knauth and Greenbie, 1997). They concluded that the source of discharge to upper Verde River springs was the carbonate aquifer north of the upper Verde River. This interpretation was largely based similarities between samples collected from the upper Verde River and the Glidden well (fig. E1). Wirt and Hjalmarsen (2000) compiled and interpreted ^{18}O , ^2H , ^3H , and ^{13}C data compiled from earlier studies, along with new samples from upper Verde River springs. These stable-isotope data were used in a mass balance calculation to estimate the relative proportion of inflow to the Verde River from the Big and Little Chino aquifers. On the basis of the mass balance results, Wirt and Hjalmarsen (2000) concluded that the Big Chino aquifer supplied at least 80 percent of the base flow in the upper Verde River. This estimate was compared with their water budget for the upper Verde River based on historical precipitation, stream discharge, ground-water levels, and pumping records. Data used in their study came from the water-quality and stream-gauge databases of the USGS, the Arizona Department of Water Resources ground-water monitoring network, National Weather Service climate records, ASU stable-isotope data (Knauth and Greenbie, 1997), and USGS databases. The different conclusions reached by the ASU and USGS studies over the origin of springs in the upper Verde River have remained a source of controversy and are a major focus of this study.

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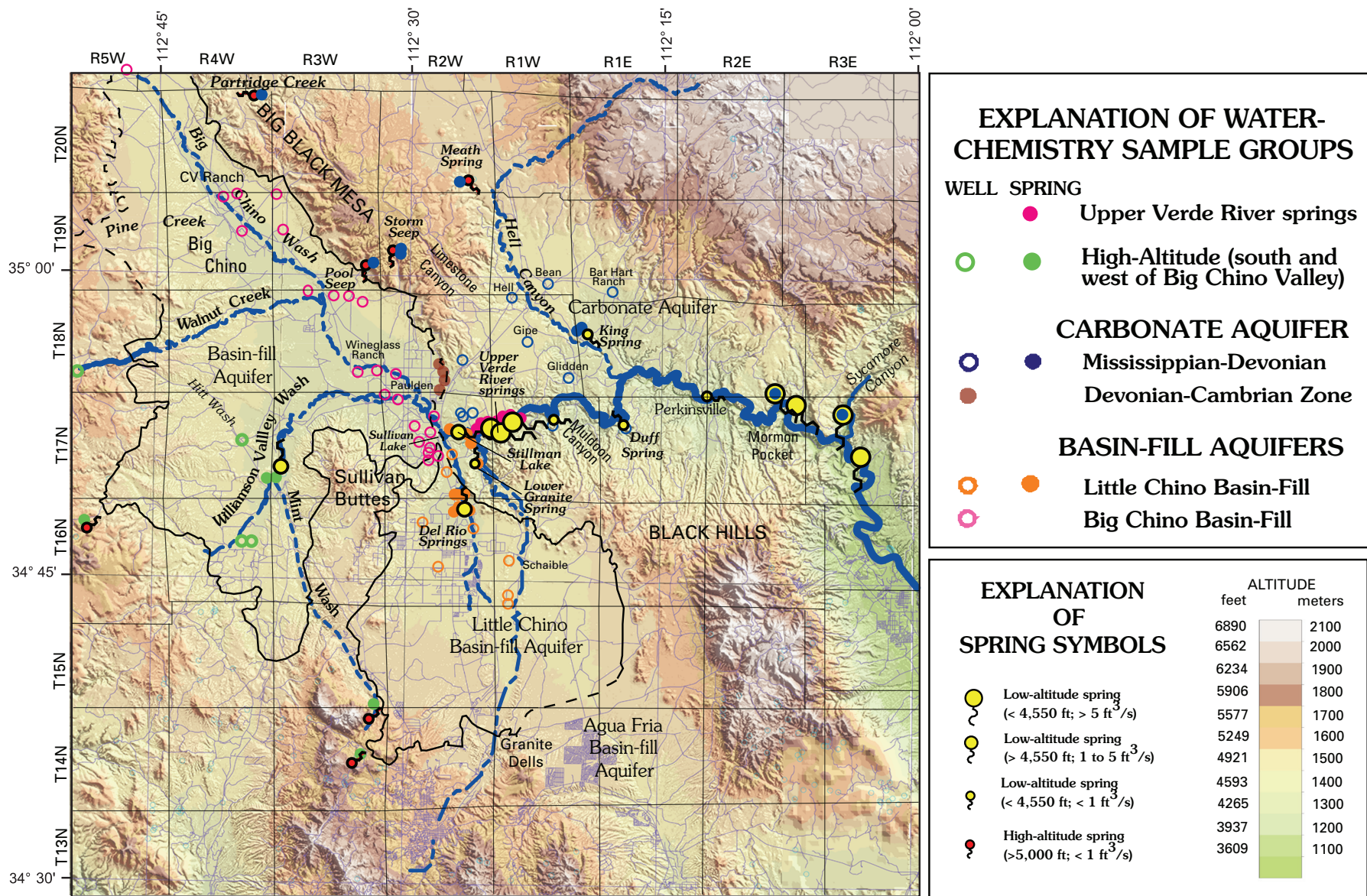
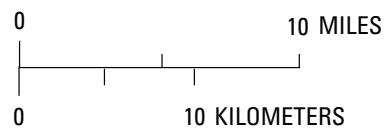


Figure E1. Major water-chemistry sample groups characterized in this study, Verde River headwaters region, Arizona. Water chemistry and isotope data are reported in Appendixes A and B, respectively. Aquifer boundaries are dashed where likely interconnected with adjacent aquifer (Wirt and DeWitt, this volume; Chapter D). Base is from 1:100,000 U.S. Geological Survey digital data.



manuscript. The following local residents also granted permission and provided access for water sampling activities: Billy Wells, David Gipe, Don Varner and Ann Gipe, Harley and Patty Shaw, Billy Wells, Ann Harrington, and the Reeves, Wagner, Smith, Prucha, Schaible, and Arnold families. Prescott National Forest, Arizona Game and Fish, and the Las Vegas, Alimeda Cattle, Kieckheffer (K4), and Hitchcock (T2) Ranches also provided access for sampling. Field support was provided at various times by Susan Lane Matthes, Ann Harrington, Eddessa Carr, Kay Lauster, and by Pam Sponholz and Shaula Hedwall of the U.S. Fish and Wildlife Service. USGS personnel who assisted the authors in the field include Betsy Woodhouse and Christie O'Day.

Methods of Investigation

Sample sites were selected to characterize aquifers, to show spatial variations in the concentrations of selected solutes of interest, to identify recharge areas, and to define changes in apparent age along major ground-water flow directions. Targeted flowpaths for sampling were chosen from water-level contour maps and water-level data (Schwab, 1995; Corkhill and Mason; 1995; Wallace and Laney, 1976; and Chapter D, this volume, figs. D6 and D7).

Sampling also targeted gaps in coverage by previous studies. Gaps in previous studies were geographic and analytical. Earlier investigations by the USGS (Wirt and Hjalmarson, 2000), and Knauth and Greenbie (1997, Arizona State University) focused on the Big and Little Chino basin-fill aquifers and major springs in the upper Verde River. Few samples had been collected from the carbonate aquifer north of Big Chino Valley and the upper Verde River, particularly in the area surrounding Big Black Mesa. Also, relatively few samples had been collected from springs and tributaries in mountain-front recharge areas such as the Bradshaw, Santa Maria, and Juniper Mountains. Knauth and Greenbie (1997) measured stable isotopes but did not analyze for major ions, trace elements, tritium, or carbon isotopes. In addition, earlier studies by the USGS did not routinely include several trace elements of interest in this study, notably boron, lithium, and arsenic.

Sampling sites, ranging from upland springs to lowland points of ground-water discharge, are grouped on figure E1, using a color and symbol scheme that is followed in subsequent figures. Strategy for sample-site selection and how samples were assigned to groups for the purpose of interpretation is explained in the following section.

Sampling Strategy

In order to characterize the water chemistry of major aquifers and springs discharging to the upper Verde River, ground-water samples were grouped by major aquifer or by altitude and geographic location (fig. E1). Major sample

groups include (a) the Big Chino basin-fill aquifer, (b) the Little Chino basin-fill aquifer, (c) the carbonate aquifer north of Big Chino Valley and the upper Verde River, (d) high-altitude areas west and south of Big Chino Valley, and (e) upper Verde River springs. These groups correspond with the hydrogeologic framework presented in Chapter D (this volume). Basin-fill aquifer samples typically include well samples and low-altitude springs near the outlets of the basins. Carbonate aquifer samples include high- and low-altitude springs and deep wells located north of the upper Verde River and Big Chino Valley. The high-altitude sample group includes shallow well and spring samples in probable recharge areas near the Bradshaw, Santa Maria, and Juniper Mountains where precipitation and runoff are the greatest within the study area. Samples from upper Verde River springs comprise their own sample group.

An important consideration was how to select samples that best represent each aquifer. In stream sampling, a standard procedure is to collect a horizontal and vertical composite of streamflow, representing a flow-weighted composite. In ground-water sampling, it is nearly impossible to collect a flow-weighted composite representing the cross-sectional width, depth, and average flow rate of the aquifer. Each well represents a point sample; or at best, a vertical composite that often does not fully penetrate the thickness of the aquifer. In addition, the problem of representatively sampling an aquifer is different for an alluvial aquifer versus a fractured rock aquifer. For these reasons, it was not possible to collect a volumetric composite at different points within each aquifer along major flowpaths. A large spring discharging from the downgradient end of an aquifer could, however, be considered a volumetric composite—as long as no substantial mixing with an adjacent aquifer has occurred upgradient from the spring.

In this study, low-altitude springs near topographical basin outlets were considered representative of outflow from the upgradient aquifer. For example, Del Rio Springs and Lower Granite Spring samples were grouped as part of the Little Chino basin-fill aquifer, and samples from King Spring, Mormon Pocket spring, and Summers Spring in Sycamore Canyon were considered part of the Mississippian-Devonian (M-D) sequence in the carbonate aquifer. In contrast, although upper Verde River springs is the largest low-altitude spring downgradient from Big Chino Valley, the springs could not be grouped as part of Big Chino basin-fill aquifer sample group because a major objective of this study was to test whether a smaller amount of mixing with the carbonate aquifer occurs prior to discharge to the upper Verde River. Thus the upper Verde River spring samples were grouped separately from Big Chino basin-fill aquifer samples. For the same reason, Stillman Lake samples initially could not be grouped with any aquifer, although the lake was subsequently interpreted to have a Little Chino source on the basis of several lines of geochemical evidence that will be presented later in this chapter.

Springs and wells north of Big Chino Valley and the upper Verde River—from Partridge Creek on the west to Sycamore Canyon on the east—were sampled to represent

the regional carbonate aquifer. In this region, there are so few wells and springs in the carbonate aquifer that nearly all available sites were sampled. There are no wells on Big Black Mesa, but four springs were sampled around its perimeter at elevations greater than 4,500 ft. Three wells and three springs were sampled between Big Black Mesa and Sycamore Canyon. Most of the carbonate aquifer samples are from the Martin Formation or overlying Redwall Limestone, which have been grouped as part of the M-D sequence of the carbonate aquifer. North of Paulden, four wells produce from the Devonian-Cambrina (D-C) zone of the carbonate aquifer beneath the Big Chino basin-fill aquifer (Chapter D, this volume). As results will show, these four samples have distinct water-quality characteristics related to differences in the geology and have been interpreted as a subgroup of the carbonate aquifer. Throughout this report, the two stratigraphic intervals are referred to as the D-C zone and the M-D sequence of the carbonate aquifer.

High-altitude springs and major tributary inflows to the Big Chino and Williamson Valley basin-fill aquifer include perennial (or spring-fed) reaches in lower Williamson Valley Wash and Mint Wash, shallow wells in the Williamson Valley and Walnut Creek watersheds, and several high-altitude springs at elevations greater than 4,500 ft in the Bradshaw, Santa Maria, and Juniper Mountains. In general, these high-altitude samples have small catchment areas. An exception is the perennial reach of lower Williamson Valley Wash, which occupies a position intermediate to high-altitude and low-altitude springs at 4,500 to 4,450 ft in elevation. The reach is downgradient of a large subbasin composed of alluvium and buried volcanic rocks, and has been interpreted as a representative composite of high-altitude recharge to Williamson Valley. Thus, samples along Williamson Valley Wash were included in the high-altitude sample group, but also could have been included as a tributary of the Big Chino basin-fill aquifer. Big Chino basin-fill wells were selected along the longitudinal valley axis between high-altitude recharge areas and the upper Verde River.

Lastly, an attempt was made to sample springs emerging from a variety of rock types. Springs in the Bradshaw and Santa Maria Mountains generally are in contact with Proterozoic granites and gneisses. Springs in the Juniper Mountains and Big Black Mesa emerge from Paleozoic carbonate rocks or Tertiary basalt flows. Perennial segments of major tributaries, such as lower Williamson Valley Wash and Walnut Creek, emerge from stream alluvium that is a composite of upgradient rock types.

Sources of alluvium in Big Chino Valley include Proterozoic igneous or metamorphic rock from the Bradshaw and Santa Maria Mountains, carbonate rock from the Juniper Mountains and Big Black Mesa, and Tertiary volcanic rocks in the basin-fill deposits, Sullivan Buttes, and surrounding upland areas. Basin-fill deposits in Little Chino Valley include most of the same rock types found in Big Chino Valley, although in somewhat different proportions. Little Chino basin-fill deposits contain a much higher fraction of volcanic extrusives, particularly latite-andesite (Chapter D, this volume). The source of alluvium in Little Chino Valley is predominantly

Proterozoic igneous or metamorphic rock from the Bradshaw Mountains and Granite Dells and Tertiary volcanic rock from Sullivan Buttes. Sediment in the northeastern part of the basin originating from Paleozoic rock in the Black Hills contains a large fraction of carbonate material. Variations in the concentrations of solutes in the basin-fill aquifers can sometimes be explained by association with certain rock types. In such instances, it generally is easier to discuss spatial variability of a few individual samples within the group, rather than to add a new subgroup or classification.

Field Methods

Well and spring discharges were monitored at least 20 minutes prior to sample collection to allow stabilization of water temperature, specific conductance, pH, and dissolved oxygen. Well samples were collected after at least three well volumes had been purged or after field measurements had stabilized, or both—as prescribed by USGS standard sampling methods (Wilde and others, 1999). Livestock and irrigation wells typically were sampled after running a generator-operated pump overnight (12 hours or longer), in cooperation with the rancher. Windmills were sampled from outlet pipes following sufficiently windy conditions, that is if it was observed that the blades were turning and the stock tank was overflowing. No well samples were collected from stagnant stock tanks, because substantial evaporation could have occurred.

Small diffuse springs and spring-fed pools of water were problematic to sample for a variety of reasons. Springs discharging to a gaining stream typically emerge through the streambed and mix with streamwater. This makes it difficult to sample the inflow directly or to get a flow-weighted composite of diffuse inflows through a gaining reach. Most of the inflow to upper Verde River springs occurs through the streambed. The eight samples collected June 17-18, 2000 (Appendix A), each represent a discrete inflow that had not yet entered or mixed with the Verde River. Thus, averaged values for the group of samples cannot be considered a true volumetric composite. Moreover, if a spring-fed pond is large and stagnant or slow-moving (such as Stillman Lake or King Spring) then it often was difficult to identify the point of ground-water inflow and the best sampling location. In these cases, evaporation and chemical reactions with atmosphere may affect the water chemistry. Spring sampling locations were selected by looking for sites with clear water (not cloudy), visible current, and relatively low dissolved oxygen and water temperature values. In a few instances, springs appeared currentless or stagnant (notably King Spring, Stillman Lake, an unnamed spring in Tucker Canyon, and Meath Spring) and it was not always possible to find field evidence for ground-water inflow. Consequently these spring data were interpreted with the knowledge that evaporation could have occurred prior to sampling. In addition, water chemistry of some of these high-altitude springs appears to vary seasonally. An understanding of field-sampling conditions was an important consideration in the interpretation of the stable-isotope results.

Analytical Methods

Separate aliquots of ground-water samples were analyzed for major and trace ions, ^{18}O , ^2H , ^3H , ^{13}C , and ^{14}C . Aliquots for cation analyses were filtered in the field using a cellulose-nitrate 0.45-micron pore-size filter and acidified using ultrapure nitric acid. Aliquots for anion analyses were filtered with no acidification. On rare occasions that spring water was visibly cloudy, isotope samples were filtered. Isotope samples were always unacidified and usually unfiltered. Alkalinity was measured in the field by incremental titration with 1.6N H_2SO_4 (Wilde and others, 1999).

Major- and trace-element concentrations were measured at the USGS Mineral Resources Program laboratory in Denver, Colorado. Major elements were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Briggs and Fey, 1996) and by inductively coupled plasma-mass spectrometry (ICP-MS; Lamothe and others, 1999). Concentrations of chloride, bromide, and fluoride were determined by ion chromatography (d'Angelo and Ficklin, 1996). Analytical detection limits by laboratories used in this study are reported in Lamothe and others (1999) and d'Angelo and Ficklin (1996). Analytical results for major and trace-element chemistry for this and other USGS Verde River watershed studies are reported in Appendix A, grouped by major aquifer or geographical region.

Samples for ^{18}O , ^2H , ^{13}C , ^{14}C , and ^3H were analyzed by the Laboratory of Isotope Geochemistry at the University of Arizona in Tucson, Arizona. Analyses for stable isotopes of oxygen and hydrogen were performed by mass spectrometer (Craig, 1957; Coleman and others, 1982; Gehre and others, 1996). Isotopic data, grouped by aquifer or geographical region, are reported in Appendix B.

Samples for ^{14}C analysis were collected in 50-liter plastic carboys with minimal headspace and kept indoors to minimize temperature changes and to avoid exposure to direct sunlight. It usually was impractical to filter large volumes of water in the field; but if the water had obvious cloudiness from suspended material, it was filtered with a 0.45-micron pore-sized filter capsule. The carboys were transported to the University of Arizona (UA) Laboratory of Isotope Geochemistry within 72 hours of collection. At the UA laboratory, dissolved inorganic carbon was separated from the large volume of water by precipitation as barium or strontium carbonate (BaCO_3 , or SrCO_3 , respectively). The ^3H , ^{13}C , and ^{14}C activities were determined by liquid scintillation counting (Polach and others, 1973; , 1996). In several instances where site access for large sample volumes was poor, 1-liter samples were submitted for ^{14}C analysis by accelerator mass spectrometry (AMS) at the Arizona AMS Laboratory at the University of Arizona, Tucson (http://www.physics.arizona.edu/ams/education/ams_principle.htm). Accelerator mass spectrometry costs about twice as much as liquid scintillation, but requires a substantially smaller volume of precipitate and has a smaller uncertainty of < 0.3 percent modern carbon (pmc).

The reported analytical precision for tritium generally was between 0.6 and 0.9 tritium units (TU) with a detection limit of about 0.5 TU, depending on the length of counting and the level of enrichment. Analytical detection limits varied from 0.4 to 1.2 TU, depending upon the counting time and activity of each sample. The analytical uncertainty for ^{14}C was reported as < 0.8 pmc for liquid scintillation (Christopher J. Eastoe, written commun., 2003).

Isotope Characterization and Apparent Age-Dating Techniques

The following is an overview of the stable-isotope and radioactive-isotope techniques used by this study. Stable isotopes were used to identify sources of water, to estimate ground-water quality changes along a flowpath, to determine the amount of mixing (if any), and to identify water that has undergone evaporation since precipitation in the source area.

Radioactive isotopes were used to indicate the amount of time that ground water has been isolated from the atmosphere. Abundances of radioactive isotopes are expressed as activities because counting methods measure energy emissions from a given volume of sample, rather than the concentration of an individual isotope. The activity of a radioactive nuclide is related to the number of atoms, its decay constant, and the counting efficiency of the radiation detector.

Hydrogen and Oxygen Stable Isotopes

The isotopic composition of the hydrogen (^1H and ^2H) and oxygen (^{16}O and ^{18}O) in the water molecules of the ground water and surface water is used in hydrologic studies to determine sources of water, to trace water along a flowpath, and to identify water that has undergone evaporation since precipitation in the source area (Coplen, 1993; Coplen and others, 2000). These isotopes are particularly useful in tracing ground-water flowpaths, because they are part of the water molecule and can be assumed to behave conservatively once the water has reached the saturated zone and no longer has contact with the atmosphere. Evaporation and condensation of atmospheric precipitation and moisture in the unsaturated zone are the most significant physical processes that affect the proportions of these isotopes.

Isotopes are atoms of the same element that differ in mass because of a difference in the number of neutrons in the nucleus (Fritz and Fontes, 1980). For example, deuterium (^2H) is hydrogen with one proton and one neutron in the nucleus and is distinguished from hydrogen (^1H) that has one proton and no neutrons in the nucleus. Stable-isotope ratios are expressed in per mil units, or parts per thousand (‰), to represent the deviation of the isotope ratio to a reference standard using delta notation (δ), according to equation 1:

$$\delta = \left(\frac{R_x}{R_{\text{std}}} - 1 \right) 1,000 \quad (1)$$

where

R_x = ratio of isotopes in the sample, and
 R_{std} = ratio of isotopes in the standard.

R is the measured isotopic ratio. Per mil values are presented relative to a standardized reference compound, which is different for different isotopes. In this report the standardized reference compound used is Vienna Standard Mean Ocean Water (SMOW) for hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) (Coplen, 1994). The delta symbol is followed by the chemical symbol for the heavier isotope of the isotope pair (for instance $\delta^{18}\text{O}$, because ^{18}O is heavier than ^{16}O). Larger (or less negative) values show the sample to be enriched in the heavy isotope species relative to the standard, and smaller (or more negative) values show the sample to be depleted in the heavy isotope species relative to the standard.

Isotopic variations in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ usually are covariant because they are part of the water molecule. The vapor pressure of water containing the lighter isotopes of hydrogen and oxygen (^1H and ^{16}O) is greater than that of water containing the heavier isotopes, deuterium, and oxygen-18 (^2H and ^{18}O). Therefore, ^1H and ^{16}O evaporate more readily than ^2H and ^{18}O . Atmospheric water vapor becomes progressively depleted in the heavier isotopes as the vapor travels from near the equator toward the poles, from the coast inland, or from lower to higher altitudes. In general, the isotopic composition of precipitation varies globally according to the World Meteoric Water Line (WMWL) (Craig, 1961), computed by equation 2:

$$\delta^2\text{H (per mil)} = 8 \delta^{18}\text{O (per mil)} \pm 10 \quad (2)$$

Equation 2 shows that the isotopic composition of globally averaged precipitation typically varies with a slope of 8 on plots of $\delta^{18}\text{O}$ at ‰. The intercept, known as the deuterium excess, has been observed to vary widely depending on local climatic conditions (Dansgaard, 1964). During the kinetic fractionation effect of evaporation, the isotopic composition of residual water is shifted toward greater enrichment of ^2H and ^{18}O as a function of temperature, humidity, salt concentration, and other factors (Coplen, 1993). A slope between three and less than eight is typical of water that has undergone substantial evaporation (Ingraham, 1998, p.93; Coplen, 1993, p. 235). In Arizona, significant variations in the ^2H and ^{18}O of precipitation and subsequent runoff are caused by (1) seasonal variability between winter storms and summer monsoons, (2) local differences in altitude, and (3) evapotranspiration of surface-water runoff prior to direct recharge (Kalin, 1994; Van Metre and others, 1997, p. 29-30; and Wright, 2001). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ contents of a ground-water sample are composites of prevailing climate conditions in the recharge area. So far as recharge and discharge conditions are averaged over the long-term, stable-isotope ratios in ground water discharging near the distal end of the aquifer (in the absence of evaporation) are expected to remain constant through time.

Tritium

Tritium (^3H) has a half-life of 12.42 years (Lucas and Unterweger, 2000) and is produced naturally in the atmosphere by cosmic-ray bombardment of nitrogen and oxygen in the atmosphere (International Atomic Energy Agency, 1994). From 1952 to 1969, large amounts of tritium were released into the atmosphere by the testing of thermonuclear weapons. The average tritium activity for Arizona precipitation during the period 1962–1965 (International Atomic Energy Agency, 1994) was 1,140 tritium units [one tritium unit (TU) = one ^3H atom per 10^{18} H atoms]. Since the end of above-ground testing in 1963, the tritium activity in precipitation has decreased as a consequence of radioactive decay and atmospheric fallout. Background levels of tritium in southern Arizona have ranged from about 5 to 10 TU since 1994 (C. J. Eastoe, oral commun., 2004). For the timeframe of this study, water with detectable tritium probably has been recharged since 1953 or else has mixed with a fraction of water that is post-1953. Tritium in ground water recharged before 1953 has now decayed to an activity that is below a detection limit of 0.4–0.7 TU. Water exceeding modern background levels of 5 to 10 TU has been in equilibrium with the atmosphere since 1953 (Ingraham, 1998) and before 1994 (C. J. Eastoe, oral commun., 2004). A tritium activity below 5 TU is ambiguous in that some of the ground water could have recharged since 1953 and mixed with predominantly older water. Because of decreasing levels of tritium in modern precipitation and uncertainties due to possible mixing, in this study, tritium was not used to date ground water precisely. Tritium activities primarily are used to indicate areas where recent recharge may be occurring and to assist with the interpretation of ^{14}C results.

Carbon-13 and -14

Carbon has two stable isotopes (^{12}C and ^{13}C) and one radioactive isotope (^{14}C). Carbon-14 has a half-life of 5,730 years, making it a useful dating tool for ground water that is thousands of years old (Fritz and Fontes, 1980). Carbon-14 undergoes radioactive decay to ^{14}N so that once isolated from the atmosphere, the amount of ^{14}C decreases in direct relation to its half-life. Like tritium, ^{14}C is produced in the upper atmosphere by interaction of cosmic rays, and also was introduced in large amounts by nuclear weapons testing. Inorganic carbon enters the ground water via recharge of precipitation, dissolution of CO_2 in the unsaturated zone, and dissolution of carbonate minerals. Dissolved bomb-related ^{14}C may mix with older water, causing ages to appear younger if not corrected. The initial activity of ^{14}C and the abundance nonradioactive carbon ($\delta^{13}\text{C}$) in the recharge area, and at a downgradient point in the flow system, must be known or estimated to date the carbon and estimate ground-water ages.

Carbon-13 in ground water provides insight into sources of carbon and carbonate reactions in the flow system. Also, $\delta^{13}\text{C}$ data are used to adjust ground-water ages determined by modeling of ^{14}C data. Carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$ values, or $\delta^{13}\text{C}$)

reflect the conditions of the unsaturated zone and the type of substrate through which the water has flowed. The range of $\delta^{13}\text{C}$ in ground water is largely determined by the $\delta^{13}\text{C}$ of soil gas and reactions of carbonate minerals in the aquifer (Bullen and Kendall, 1998). Oxidation of organic matter and plant respiration in the soil zone introduces relatively light carbon. Dissolution of carbonate rocks introduces relatively heavy carbon. The $\delta^{13}\text{C}$ is measured against a standard, which is a marine fossil belemnite of the Cretaceous Peedee Formation in South Carolina. The ratio of dissolved carbonate species in the ocean (and most marine carbonate rocks) is typically about 0‰.

The primary source of $\delta^{13}\text{C}$ in ground water is from CO_2 in the soil atmosphere of the recharge zone (Bullen and Kendall, 1998). Soil gas $\delta^{13}\text{C}$ results from atmospherically derived ($\delta^{13}\text{C} = -7\text{‰}$) and microbially respired CO_2 . The contribution of carbon as dissolved inorganic carbon from precipitation is negligible for most catchment systems (Bullen and Kendall, 1998). Few $\delta^{13}\text{C}$ soil gas values for arid areas have been reported. A mean value of $-15.12 \pm 2.88\text{‰}$ for five samples near Tucson, Arizona was determined by Wallick (1973, p. 122). Also, $\delta^{13}\text{C}$ of CO_2 in desert soil near Tucson averaged -20‰ (Parada, 1981). Partial pressure of CO_2 (P_{CO_2}) values reported in that study ranged from 0.001 to 0.05 atmospheres. Values of -15 to -19‰ have been measured for the soil gas of arid west Texas (Pearson and Hanshaw, 1970). Soil-gas samples collected from the Dripping Springs basin in central Arizona had a typical value of about -18.0‰ $\delta^{13}\text{C}$ (Pierre Glynn, unpub. data, oral commun., 2005).

The $\delta^{13}\text{C}$ of carbonate rock may vary slightly. Marine carbonate rocks normally have the same $\delta^{13}\text{C}$ value as dissolved ocean carbonate, but ratios can vary substantially within a single formation. For example, a 6.28‰ range in the $\delta^{13}\text{C}$ of the Mooney Falls Member of the Redwall Limestone was reported for 36 rock samples from three sites in the Grand Canyon and six sites along the Verde River between Chino Valley and Perkinsville (Muller and Mayo, 1986). The overall average for the nearly pure limestone samples was -1.85‰ and ranged from a maximum of $\pm 2.44\text{‰}$ and a minimum of -3.84‰ . The $\delta^{13}\text{C}$ of the Devonian Martin Limestone is unknown, but it is reasonable to assume that it should be similar to the overlying Redwall Limestone of Mississippian age. In the headwaters area, the main mineral carbon sources include limestone and dolomite, as well as secondary calcite deposited as pedogenic carbonate in unconsolidated sediments or as fracture fillings within volcanic rocks.

Water-Quality Sampling Results

For this study, 64 water samples were analyzed for concentrations of major ions and selected metals, and ratios of stable isotopes of oxygen ($\delta^{18}\text{O}$), hydrogen (^2H , or δD), and carbon (^{13}C); and for tritium (^3H). Fourteen samples were analyzed for carbon-14 (^{14}C). These new data are interpreted

here in combination with earlier USGS data compiled by Wirt and Hjalmarsen (2000) and the $\delta^{18}\text{O}$ and δD data of Knauth and Greenbie (1997).

From 1986 to present, a total of 91 water samples have been analyzed for concentrations of major ions in the upper Verde River watershed by the USGS (Appendix A). About 90 percent of these samples were analyzed by atomic emission spectroscopy for trace elements that routinely occur at the parts per million level. About 60 percent of the sample group was analyzed using mass spectroscopy, which has lower detection limitations for trace elements occurring at parts per billion levels. Consequently, there are fewer analyses available for As than for B and Li. In addition, a total of 124 well and spring samples were analyzed for stable isotopes (Appendix B). Sample results in Appendices A and B have been grouped according to the strategy outlined in the section on "Sampling Strategy" and outlined in the explanation of figure E1.

Results of major-ion, trace-element, stable-isotope, tritium, and carbon isotope data are presented sequentially in this section. In the end of the chapter, these multiple lines of evidence will be integrated by looking at variations in the geochemistry along selected ground-water flowpaths from upper Big Chino Valley to Paulden through the basin-fill aquifer, and from Paulden to upper Verde River springs through the carbonate aquifer.

Major-Ion Chemistry

Trilinear plots (Piper, 1944) are used to show relative proportions of major cations and anions, reported in percent milliequivalents per liter (% meq/l). The two trilinear plots for samples from the major aquifer groups and major springs discharging to the upper Verde River (fig. E2) show predominantly calcium-bicarbonate waters with variable proportions of magnesium and sodium. In general, calcium (Ca) is the predominant cation, and bicarbonate (HCO_3^-) is the predominant anion. Sample groups having a relatively large degree of visual scatter are plotted on figure E2A; groups that cluster more tightly are plotted on figure E2B.

For all of the basin-fill and high-altitude spring samples (fig. E2A); the major cations are Ca (30 to 70% meq/l) and magnesium (Mg) (15 to 65% meq/l), with relatively small amounts of sodium (Na) and potassium (K) (5 to 30 % meq/l). The variation in proportions of major ions in the Big and Little basin-fill aquifers and the high-altitude springs of the Bradshaw, Santa Maria, and Juniper Mountains is attributed to the ground water having contact with a wide variety of rock types; hence, a more variable chemistry. Based on of the range of major-ion proportions, it is not possible to distinguish the Big Chino basin-fill aquifer from the Little Chino basin-fill aquifer, nor is it possible to distinguish basin-fill aquifer samples from high-altitude springs and tributaries, although some of Big Chino basin-fill samples have slightly higher concentrations of chloride (Cl).

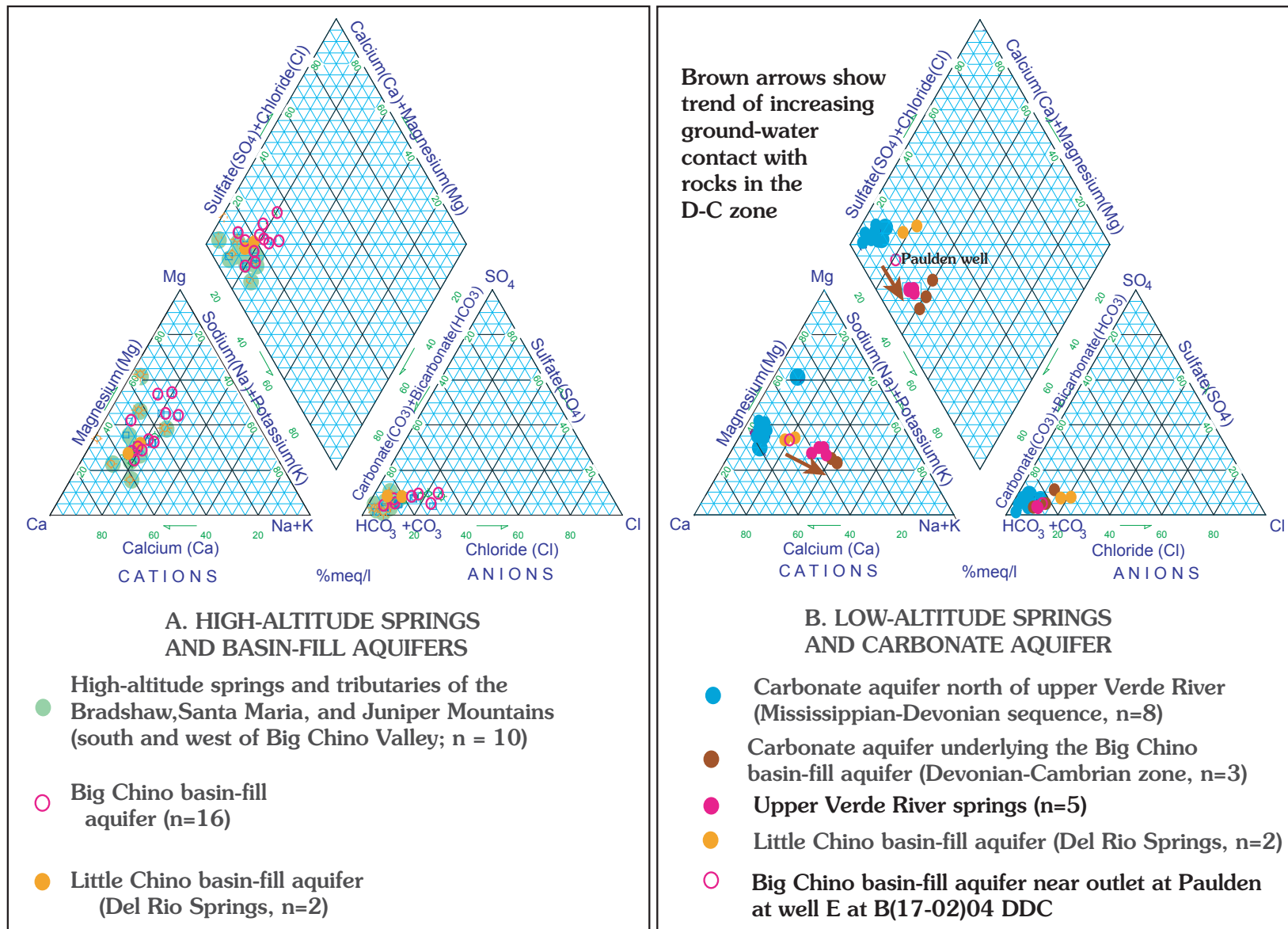


Figure E2. Trilinear diagrams (Piper, 1944) showing major-ion proportions in percent milliequivalents per liter (%meq/l). Plot A shows proportions for high-altitude springs and basin-fill aquifer; plot B shows proportions for low-altitude springs and the carbonate aquifer. Samples plotted have cation-anion balances within 5 percent. Data are reported in Appendix A; n, number of samples.

On figure E2B, the tighter clustering for upper Verde River springs is attributed to repeated sampling of a single low-altitude spring location, or in the case of the carbonate aquifer, to the two carbonate aquifer subgroups having little spatial variation in major-ion chemistry. Samples from the M-D sequence of the carbonate aquifer (blue circles, fig. E2B); plot in a fairly tight cluster on the left side of the diamond-shaped graph. The major cation is Ca (55 to 60% meq/l), followed by Mg (35 to 45% meq/l), with less than 10% meq/l of Na and K.

In contrast, the D-C zone of the carbonate aquifer underlying the Big Chino basin-fill aquifer (brown circles, fig. E2B) has distinct major-ion proportions, plotting to the lower right of all other sample groups. The major cation for this sample group is Na, rather than Ca. These samples have among the highest concentrations of Na, Cl, sulfate (SO_4), and silica (Si) in the study area, as shown by the brown box- and whisker plot of major-element concentrations (fig. E3A). The samples were collected from four wells >285 ft in depth northeast of Paulden and east of Wineglass Ranch (B-18-02, sections 21, 27 and 28; see Appendix A for well depths). Each well penetrates a thin veneer of basin-fill sediment into the underlying Paleozoic rocks (DeWitt and others, this volume) and is interpreted as producing from the water-bearing zone near the base of the Martin Formation or top of the Bright Angel Shale.

Like the four wells in the D-C zone, ground water from upper Verde River springs also discharges near the base of the Martin Formation. Water from upper Verde River springs has nearly equal major-ion proportions of Ca, Mg, and Na, which plot intermediate to those for the Big Chino basin-fill aquifer and the D-C zone. A brown arrow shows the evolution of increasing water-rock interaction, from the outlet of Big Chino basin-fill aquifer at well B(17-02)04 DDC toward samples from upper Verde River springs and the D-C zone. The change in major-ion proportions primarily results from an increase in Na, Cl, SO_4 , and Si concentrations as opposed to a small increase in the Ca concentration (fig. E3A). The range of Ca values for upper Verde River springs compares more closely with the range of Ca values for the Big Chino basin-fill aquifer than with the range for the D-C zone. Ground water of the D-C zone is moderately mineralized and characterized by consistently higher concentrations of Na, K, Cl, SO_4 , and Si, than all other sample groups (figs. E2B and E3A). Intermediate concentrations of these elements in ground water discharging to upper Verde River springs may result either from water-rock interaction of Big Chino basin-fill ground water as it travels through the D-C zone or from mixing of the Big Chino basin-fill aquifer with ground water from the D-C zone. Both of these hypotheses and the geology of the outlet flowpath are addressed next.

Trace-element Chemistry

Trace elements are useful indicators of water-rock reactions. In this section, box- and whisker plots (SAS Institute, 1998) were used to visually summarize the differences in

selected major-ion and trace-element concentrations for each of the sample groups of interest. The elements shown on fig. E3 (with the exception of Ca) were selected to best illustrate the differences among sample groups. Calcium concentrations are shown to provide a frame of reference, because with few exceptions it is the major cation. The majority of analytes which were not selected typically have overlapping ranges in concentrations that vary little among the different groups (much like Ca). The box- and whisker plots show the median and 10th, 25th, 75th, 90th percentiles for each statistical grouping. Outlier values above the 90th and below the 10th percentiles were omitted. In all three plots, the vertical axis has a log scale.

Marine Shale Origin of Arsenic, Lithium, and Boron

With the exception of samples from upper Verde River springs and the D-C zone, dissolved arsenic (As), boron (B), and lithium (Li) concentrations are relatively low throughout most of the study area (fig. E3B and 5.3C). The source of these elements is of particular interest because they indicate the nature of water-rock interactions along the major ground-water flowpath from the outlet of the Big Chino basin-fill aquifer near Paulden to upper Verde River springs. Perennial flow in the upper Verde River emerges from the D-C zone, near its confluence with Granite Creek. Discharge to upper Verde River springs (river mi 2.3 to 2.9) is from the lower Martin Formation (Devonian), which overlies the the Chino Valley Formation (Devonian?) above the Tapeats Sandstone (Cambrian). Box- and whisker plots of dissolved As, Li, and B for the upper Verde River springs sample group are higher than all other sample groups, with the exception of the four wells penetrating the D-C zone. Well samples from the D-C zone have concentrations of 33–38 $\mu\text{g/L}$ As, 330–460 $\mu\text{g/L}$ B, and 54–86 $\mu\text{g/L}$ Li, compared with those from upper Verde River springs of 17–29 $\mu\text{g/L}$ As, 136–270 $\mu\text{g/L}$ B, and 28–49 $\mu\text{g/L}$ Li (fig. E3B; Appendix A). In addition, As, Li, and B values for the D-C zone correlate positively with Na, K, Cl, SO_4 , and Si, values (fig. E3A). Shales of marine or lacustrine origin are a possible sedimentary source for all of these elements. Silicate minerals in igneous rocks are a possible source of Na, K, and Si.

The occurrence of elevated As, Li, and B is unusual, because few sedimentary rocks contain this suite of trace elements. The three elements typically are found together in volcanic gases and geothermal water (Hem, 1985; Shaw and Sturchio, 1991); however, there are no known geothermal springs in the study area. In addition, volcanic rocks in the study area contribute relatively low concentrations of these trace elements to water of basin-fill aquifers and do not appear to be a major source. Ground water at Del Rio Springs, for example, has had extensive contact with a variety of volcanic rocks in the Little Chino basin-fill aquifer, yet contains comparatively low concentrations of As, Li, and B. In contrast, ground water discharging to upper Verde River springs has had extensive contact with the D-C zone of the carbonate aquifer.

Dissolved Major and Trace-Element Concentrations, Verde River Headwaters, Arizona

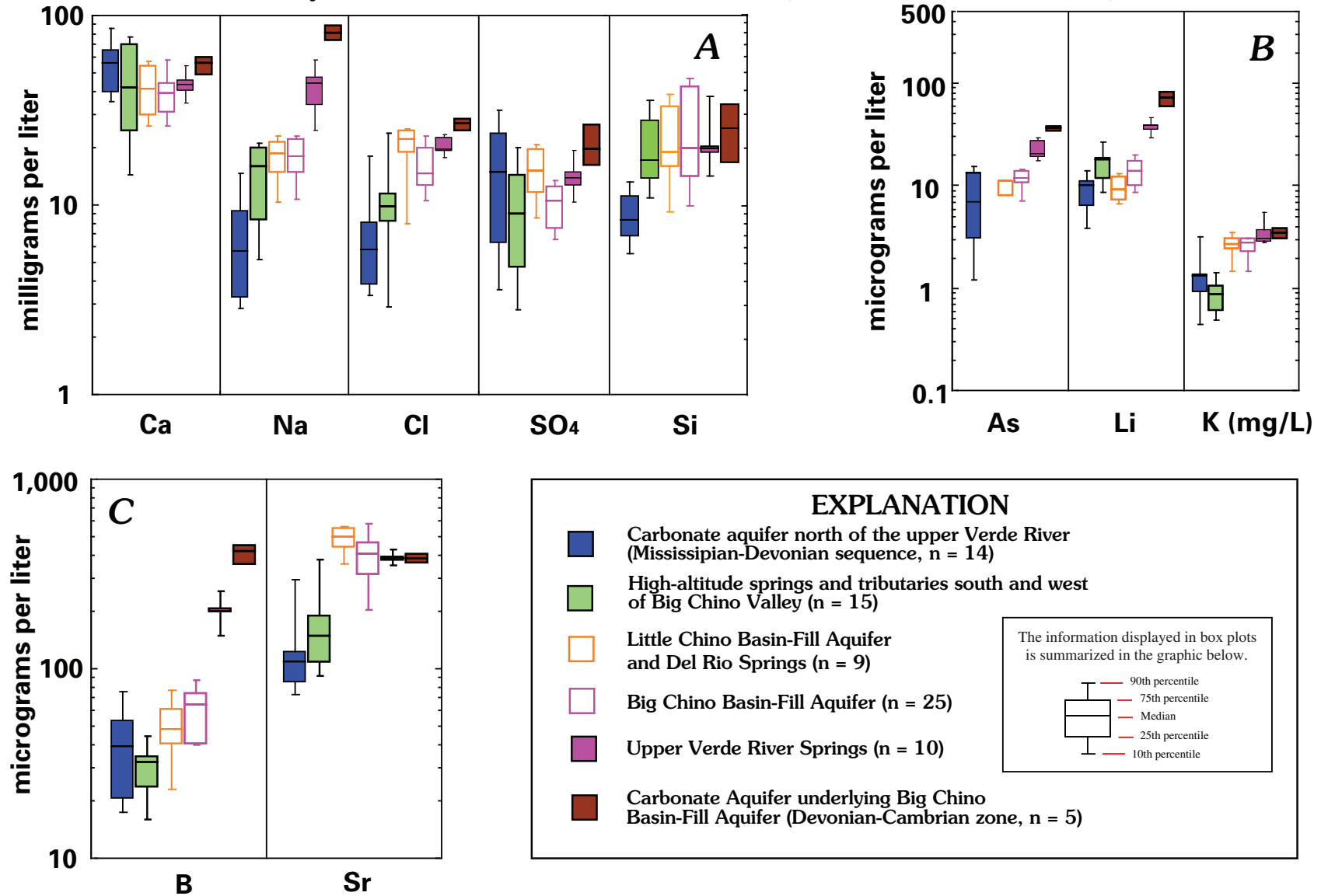


Figure E3. Box- and whisker plots (SAS Institute, 1998) of selected major and trace elements characterizing major aquifers and springs, Verde River headwaters, Arizona. Plot A, major element concentrations; Plots B and C, trace-elements concentrations. Order of box- and whisker plots is the same as in explanation; n, number of samples; all data reported in Appendix A. Not all samples were analyzed for all constituents. Outliers above and below the 10th and 90th percentile are not shown.

The Chino Valley Formation, the most likely source of these elements in the D-C zone, is a pebble conglomerate, mudstone, and siltstone unit between the Martin Formation and the Tapeats, probably of Devonian age (Hereford, 1975; Chapter D, this volume). Exposures are found near the mouth of Granite Creek and also along the base of Big Black Mesa east of Partridge Creek (Hereford, 1975). The Chino Valley Formation occupies the same stratigraphic interval and has chemical similarities to the Cambrian Bright Angel Shale (table E1), which crops out farther west in northwestern Big Chino Valley (Krieger, 1967; DeWitt and others, Chapter B, this volume, fig. B1). Potassium concentrations as high as 10.0 weight percent (as K_2O) and B concentrations as high as 280 parts per million (ppm) for the Bright Angel Shale (Miesch, unpub. data in Baedeker and others, 1998) suggest that the shale may contain a component of felsic tuff that was deposited in a shallow-water marine setting (Bowie and others, 1966, 1967; Hutcheon and others, 1998). Marine shale formed from K-rich ash is a reasonable source of As, Li, and B. These elements are present in ocean water at concentrations of 4.41 ppm B, 0.17 ppm Li, and 1.45 to 1.75 parts per billion (ppb) As (Emsley, 1991), and would tend to be concentrated by sorption to fine-grained sediment and clay.

Solid-phase concentrations as high as 8.6 weight percent K_2O in the Chino Valley Formation (Hereford, 1975) also suggest a submarine ash depositional environment similar to that for the Bright Angel Shale. We note a comparative lack of solid-phase potassium in other permeable rocks within the study area (table E1). Elevated concentrations of dissolved As, Li, and B in upper Verde River springs and well samples from the D-C zone north of Paulden suggest contact with a sedimentary unit similar in genesis to the Bright Angel Shale or Chino Valley Formation. Ground-water contact with Paleozoic-age shale would explain elevated concentrations of dissolved As, B, and Li; although solid-phase data for As and Li in Paleozoic shale are lacking.

An alternative hypothesis is that the elevated dissolved As, B, and Li could be derived from the playa deposit in Big Chino Valley. Economic deposits of boron commonly are found in playa deposits as borax (Emsley, 1991), although little is known about As or Li occurrence or behavior in a playa environment. In this scenario, ground water in contact with the playa in the Big Chino basin-fill aquifer travels along the Big Chino Fault zone and through karst of the underlying and adjoining D-C zone. Although plausible, there are no dissolved or solid-phase chemistry data from the playa deposit to directly support or refute this hypothesis. In both scenarios, ground water from the Big Chino basin-fill aquifer travels through the D-C zone to reach upper Verde River springs.

Not all ground water in the carbonate aquifer has had extensive contact with the D-C zone. Waters having among the lowest concentrations of As, B, and Li (fig. E3B) include the M-D sequence of carbonate aquifer and high-altitude springs south and west of Big Chino Valley in contact with a variety of rock types. Arsenic, B, and Li concentrations for the Big Chino basin-fill aquifer group are highest near the

southeastern end of the basin, which could be an indication of upwelling or mixing with deeper circulating ground water from the underlying carbonate aquifer near the outlet of the aquifer. On average, the Big Chino aquifer sample group contains slightly higher concentrations of As, Li, and B than samples from the Little Chino basin-fill aquifer and Del Rio Springs. The highest As, Li, and B concentrations in Little Chino ground water are found near the Granite Creek/Verde River confluence where the Chino Valley Formation is present. In general, elevated As, Li, and B concentrations provide a distinct tracer for ground water that has been in contact with the D-C zone.

Igneous and Sedimentary Sources of Strontium

Strontium (Sr) in ground water is derived from weathering of rocks undergoing weathering and dissolution in the drainage basin (Benson and Peterman, 1995; Bullen and Kendall, 1998, Bierman and others, 1998). The amount of strontium in ground water is related to the initial Sr content of rock-forming minerals and its chemical availability, which is a function of leaching, dissolution, degree of weathering, and residence time. Strontium is similar in chemistry to the alkaline-earth element calcium and replaces calcium and potassium in silicate and carbonate minerals in minor amounts (Hem, 1985). In any given catchment, Sr may be released at different rates; for example, from carbonates by dissolution, plagioclase by leaching, and clay minerals by ion-exchange processes (Bierman and others, 1998).

High concentrations of Sr are common in brines and evaporates (Hem, 1985), as well as in playa deposits of the western Great Basin (Benson and Peterman, 1995; Lin, 1996). Strontium concentrations probably are elevated in the vicinity of playa deposit near the center of Big Chino Valley, although both water and solid-phase data are lacking. Rocks having the lowest concentrations of Sr are the Paleozoic Redwall Limestone and Martin Formation, with less than 100 ppm. Other Paleozoic units have slightly higher Sr concentrations, but generally are less than 220 ppm. Most Proterozoic rocks are moderately low in Sr, with between 200 and 500 ppm.

With the possible exception of the playa, strontium-rich volcanic rocks are the major source of dissolved Sr in the headwaters study area. Strontium-rich rocks in the study area include Tertiary basalts and lati-andesite, with the Hickey basalt averaging 1,700 ppm (table E1). Two Sr-rich volcanic units are exposed north of Del Rio Springs and the area surrounding Sullivan Lake and the Sullivan Buttes. These are 4.5-Ma basalt flows near Paulden with an average concentration of 660 ppm Sr; and the Sullivan Buttes lati-andesite in northern Little Chino Valley with an average concentration of 960 ppm Sr (table E1). Water samples from Del Rio Springs, Lower Granite Springs, and Stillman Lake are substantially elevated in strontium, having dissolved concentrations ranging from 460 to 620 $\mu\text{g/L}$ (fig. E3C). Dense plugs of Sullivan Buttes lati-andesite that become more abundant in the northern part of the basin are the most likely source of dissolved Sr at

Table E1. Chemistry of major rock types exposed in Verde River headwaters region, Arizona. Solid-phase rock data from U.S. Geological Survey PLUTO database, except as noted.

(nd, not determined; <, less than; n, is number of samples)

Map unit	Rock type	Number of samples (n)	weight percent									parts per million				
			Silica as SiO ₂	Aluminum as Al ₂ O ₃	Iron as Fe ₂ O ₃ ⁵	Iron as FeO	Magnesium as MgO	Calcium as CaO	Sodium as Na ₂ O	Potassium as K ₂ O	Manganese as MnO	Carbon Dioxide as CO ₂	Barium	n	Strontium	n
Tby	Younger basalt	47	50	15.7	4.0	7.2	6.7	9.3	3.3	1.3	0.17	0.34	470	8	660	32
Tbo	Older basalt	3	51	14.1	0.0	0.0	6.9	8.5	3.1	1.5	0.14	0.02	540	2	960	3
Thb	Hickey basalt	56	50	14.4	5.3	4.5	7.7	8.6	3.4	1.9	0.14	0.06	1340	45	1700	47
Tla	Sullivan Buttes latite andesite ¹	60	60	14.1	3.5	2.5	4.2	5.4	3.0	4.4	0.08	0.19	1660	54	960	60
Ps	Supai, undivided	3	nd	6.4	1.6	nd	6.7	9.7	0.4	2.4	0.05	nd	270	3	163	3
Mr	Redwall Limestone ²	21	1	<0.010	0.1	nd	6.0	49.1	<.15	<.02	0.03	44.84	26	18	61	23
Dm	Martin Formation ²	9	2.8	<0.010	0.4	nd	20.3	29.9	<.15	<.02	0.02	46.10	18	8	74	9
Dcv	Chino Valley Fm ³	10	39	10.2	2.9	0.6	9.1	12.9	<0.2	5.2	0.05	19	nd	0	nd	0
Cba	Bright Angel Shale ⁴	16	53	18.0	5.0	0.7	1.0	0.9	0.3	8.8	0.05	0.36	510	16	219	16
Ct	Tapeats Sandstone	33	73	2.3	0.7	0.1	0.3	1.6	0.1	1.0	0.01	0.15	120	33	119	33
Cm	Muav Formation	32	18	3.2	1.6	1.4	5.3	22.0	0.5	1.8	0.12	nd	360	44	162	44
Yg	1.4-Ga plutons ²	4	69	13.9	4.1	nd	0.9	2.3	2.7	4.9	0.14	nd	840	4	242	4
Xfg	1.7-Ga felsic plutonic rocks ²	9	70	14.3	2.7	nd	0.8	1.6	3.3	4.9	0.07	nd	720	7	287	9
Xmg	1.7-Ga mafic plutonic rocks ²	41	55	15.5	5.0	5.7	5.5	7.7	2.9	1.3	0.15	nd	580	27	497	27
Xfv	1.7-Ga felsic metavolcanic rocks ²	3	68	13.7	3.0	4.4	1.1	2.2	4.7	1.1	0.07	nd	220	1	244	2
Xmv	1.7-Ga mafic metavolcanic rocks ²	80	52	15.5	3.1	9.2	4.7	7.4	3.1	0.6	0.19	nd	360	55	294	73

¹Tyner (1984); Ward (1993)

²DeWitt, unpub. Data (2002)

³Hereford (1975)

⁴Mean boron concentration for Bright Angel Shale is 180 ppm (n = 23); lithium concentration for one sample is 220 ppm.

⁵Bold value indicates percent total iron expressed as FeTO₃

Del Rio Springs (460 to 540 $\mu\text{g/L}$). Ground water discharging to Stillman Lake and lower Granite Creek has slightly higher dissolved Sr concentrations (540 to 620 $\mu\text{g/L}$), which are acquired through contact with fractured volcanic rocks along the flowpath between the Little Chino basin-fill aquifer and the Granite Creek confluence area. In addition to water-rock contact with lati-andesite, Sr concentrations at Stillman Lake and lower Granite Spring could be partly derived from the 4.5-Ma basalt flow exposed at Sullivan Lake.

In general, dissolved Sr concentrations greater than about 350 $\mu\text{g/L}$ probably indicate exposure to Tertiary volcanic rock, although the playa deposit in Big Chino Valley should not be ruled out as a possible source in that location. Direct analytical evidence to support or eliminate a playa source of strontium is not available. No ground water has been sampled directly from the playa deposit, nor are there solid-phase Sr analyses from well cuttings. The maximum concentration of 720 $\mu\text{g/L}$ Sr measured for the study area, however, was collected from a 334-ft well near the buried playa along Big Chino Wash south of Wineglass Ranch (well B-18-03 25cda) (Appendix A). A volcanic source of strontium is unlikely at this location, because the closest buried basalt unit is more than 200 ft below the bottom of the well (DeWitt and others, Chapter B, this volume; fig. B8).

A volcanic source of Sr is more plausible for the second and third highest Sr values in the Big Chino basin-fill aquifer sample group (fig. E3C). A moderately high value of 440 $\mu\text{g/L}$ Sr was measured near the confluence of Williamson Valley Wash with Hitt Wash (fig. E1, well B-16-04 15acd). This occurrence is downgradient from lati-andesite exposed in upper Hitt Wash (Chapter D; fig. D3). A concentration of 360 $\mu\text{g/L}$ Sr from northwestern Big Chino Valley (well B-19-03 30bcb) is downgradient from young basalt flows exposed in Tucker Canyon. The well log intercepts these basalt flows beneath several hundred ft of alluvium. In addition, much of the stream sediment deposited by Big Chino Wash contains basalt clasts from the upper part of the basin. In summary, the maximum Sr concentration for Big Chino Valley might be related to the playa deposit, but most other high concentrations of strontium appear to be related to the occurrence of igneous rocks. Better understanding of trace-element chemistry near the playa is needed.

In the area surrounding Sullivan Lake, which is the northern surface-water outlet for Del Rio Springs, Big Chino basin-fill wells have fairly high concentrations of Sr (between 400 and 620 $\mu\text{g/L}$) (Appendix A; B-17-02, sections 2, 4, 9, 10, and 15). In this area, the basin-fill aquifer consists of Sr-rich 4.5 Ma basalt inter-layered with alluvium, although other sources of Sr are possible. This area is also downgradient from the playa deposit, Sullivan Buttes, and alluvial fans predominantly composed of lati-andesite cobbles.

Water samples from upper Verde River springs contain between 346 and 440 $\mu\text{g/L}$ Sr, compared with 70 to 120 $\mu\text{g/L}$ Sr for samples from the carbonate aquifer (M-D sequence), and with 460 to 620 $\mu\text{g/L}$ for the Little Chino basin-fill aquifer (fig. E3C; Appendix A). In comparison, strontium

concentrations for the D-C zone range from 350 to 420 $\mu\text{g/L}$, closely matching the range measured for upper Verde River springs. The Sr concentration could be related either to the length of the flowpath or the residence time through Sr-rich rocks. Also, the clay-rich shale in the Chino Valley Formation may be more permeable or more easily leached than igneous rocks, in which Sr would be held in the crystalline lattice of feldspar minerals.

Strontium concentrations for upper Verde River springs are indistinguishable from those in the Big Chino basin-fill aquifer near Paulden and from the nearby D-C zone of the carbonate aquifer. The broad range of Sr concentrations shown by the box- and whisker plot for the Big Chino basin-fill aquifer (fig. E3C) is misleading, because it represents a range of values collected from well samples throughout the aquifer, rather than a volumetric composite measured at the aquifer outlet. Some Big Chino ground water is in contact with the 4.5 Ma basalt-filled paleochannel that straddles the aquifer boundary north of Sullivan Lake (Chapter D, this volume, fig. D8), which is an additional likely source of Sr. Because of difficulties in obtaining representative samples, the mean Sr concentration of ground water exiting Big Chino Valley through the carbonate aquifer is not known. Discharge to upper Verde River springs appears to lack extensive water-rock interaction with lati-andesite, which tends to produce Sr concentrations greater than 460 $\mu\text{g/L}$. Thus, a Little Chino source of ground water is unlikely. Mixing with a substantial fraction of ground water from the carbonate aquifer directly north of the upper Verde River (M-D sequence) also is unlikely based on typical dissolved concentrations of less than 120 $\mu\text{g/L}$, which would be expected to dilute or lower Sr concentrations. Ground-water contributions from Mississippian and Devonian rocks (M-D sequence) of the carbonate aquifer, if any, would need to first travel through the Devonian-Cambrian contact (D-C zone) and acquire higher concentrations of strontium and trace elements, or be so minor as not to substantially affect the water chemistry. The case for ground-water mixing will be further tested by inverse modeling in Chapter F (Wirt, this volume).

Isotope Chemistry

Evaporation and Characterization of Major Aquifers and Springs

Stable isotopes of hydrogen and oxygen in the ground water and surface water of the study area were used to (1) indicate the degree of evaporation, (2) characterize and compare the isotope composition of major aquifers and springs, (3) trace water along flowpaths, and (4) evaluate mixing. From 1986 to 2003, one hundred-thirty seven well and spring samples were collected and analyzed by three different stable-isotope laboratories (USGS in Reston, University of Arizona in Tucson, and Arizona State University in Tempe). Two standard deviation analytical precisions of 0.2‰ for $\delta^{18}\text{O}$ and 2.0‰ for δD are assumed for all of data used in this study

Table E2. Statistical summary of stable-isotope sample groups by major aquifers, springs, and surrounding upland areas.[δ , delta; Std Dev, standard deviation of the mean; ND, not determined; n, number of samples; all isotope values reported in per mil]

Sample Group	$\delta^{18}\text{O}$		$\delta^{18}\text{O}$		δD		δD		Count (n)
	Mean	Std Dev ³	Minimum	Maximum	Mean	Std Dev ³	Minimum	Maximum	
Carbonate Aquifer north of Verde River (Mississippian–Devonian) ¹	–11.5	ND	–12.0	–10.9	–82.1	ND	–85.0	–78.0	8
High–Altitude springs, tributaries, and wells (south and west of Big Chino Valley)	–10.7	0.4	–11.1	–10.0	–75.6	2.1	–79.4	–71.8	12
Big Chino Basin–Fill wells	–9.9	0.3	–10.5	–8.8	–71.5	3.0	–78.0	–65.0	35
Little Chino Basin–Fill wells ²	–10.0	0.4	–11.2	–8.9	–70.7	3.8	–78.0	–61.0	22
Carbonate Aquifer underlying Big Chino Basin–Fill Aquifer (Devonian–Cambrian zone)	–10.4	ND	–10.7	–10.3	–74.5	ND	–77.0	–74.0	7
upper Verde River springs	–10.3	0.1	–10.4	–10.1	–74.3	0.7	–75.0	–73.2	10

¹Includes Bean, Gipe, and Bart Hart wells; and Mormon Pocket and Sycamore Canyon springs. King, Meath, and Tucker springs were highly evaporated and not included.²Includes Del Rio Springs but not Lower Granite Spring or Stillman Lake.³Standard deviations not reported for sample groups < 10. In such instance, a 2-sigma analytical precision of 0.2 per mil for $\delta^{18}\text{O}$, and 2.0 per mil for δD are assumed (Kendall and Caldwell, 1998; p. 75; Christopher J. Eastoe, oral commun., 2003).

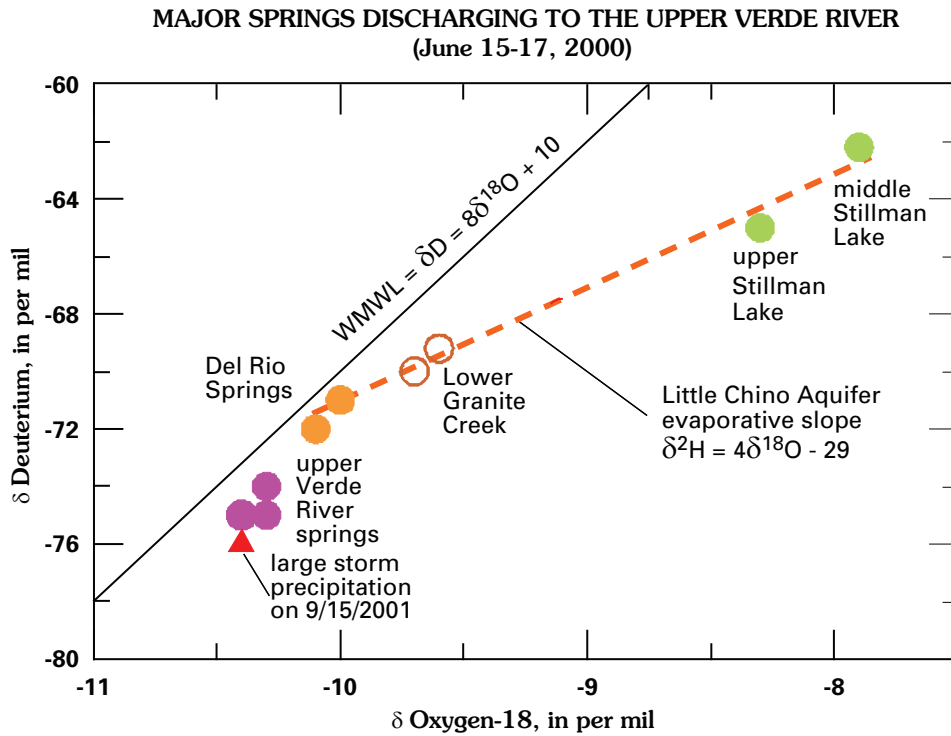


Figure E4. Graph showing δD versus $\delta^{18}O$ for springs contributing to the upper Verde River, including upper Verde River springs, Stillman Lake, Lower Granite Creek, and Del Rio Springs. All spring samples were collected June 15–17, 2000. WMWL = World Meteoric Water Line. Data are reported in Appendix B.

(Kendall and Caldwell, 1998; p. 75; Christopher J. Eastoe, oral commun., 2003).

Variations in 2H and ^{18}O were evaluated to characterize and to compare the isotope composition of low-altitude springs with ground water near the outlets of Big and Little Chino Valleys (table E2 and fig. E4). Low-altitude spring samples (fig. E4) were collected during the tracer-dilution synoptic study of June 15–17, 2000 (Chapter F, this volume). Thus, the variations in $\delta^{18}O$ and δD reflect spatial differences, as opposed to time-related differences. In general, the low-altitude spring samples plot below and to the right of the World Meteoric Water Line (WMWL).

Stillman Lake is a water-table lake that infrequently receives runoff overtopping the dam at Sullivan Lake. The lake drains through stream alluvium near the mouth of Granite Creek to the upper Verde River (Chapters A and F, this volume; fig. A15). Unlike Sullivan Lake, which changes greatly in size in response to local runoff (of lack thereof); the water

surface at Stillman Lake stays fairly constant through droughts and immediately following floods. Based on the author's observations over the past decade, the surface of Stillman Lake during low-flow conditions appears to have varied by less than a foot. Because all samples on figure E4 were collected following an extended period of little if any rainfall (U.S. Geological Survey, 1999–2003), it is unlikely that the lake samples are a mixture of ground water and surface-water runoff.

Water in Stillman Lake has a substantial residence time and experiences a considerable amount of evaporation. Samples from Stillman Lake, Granite Creek, and Del Rio Springs plot along a dashed regression line with a slope of 4, indicative of water that has undergone evaporation. Samples with the greatest length of exposure to the atmosphere are progressively enriched in 2H and ^{18}O along the regression line from Del Rio Springs (least evaporated), to Lower Granite Spring (intermediate), and Stillman Lake (most evaporated). The $\delta^{18}O$ and δD values for upper Verde River springs ($n = 6$) are substantially

more depleted than the least evaporated samples from Del Rio Springs and appear to be derived from a different aquifer source.

To evaluate whether the Stillman Lake samples are a mixture of residual surface-water runoff from wetter conditions and ground water, local precipitation was collected. During the summer of 2001, roof runoff was collected by a local resident of Chino Valley from several rain storms. A composite of several small thunderstorms from that monsoon season was highly evaporated ($\delta^{18}\text{O} = -3.3\text{‰}$ and $\delta\text{D} = -28\text{‰}$). The composite precipitation plots off the scale of the graph, on the extension of the dashed regression line for the Little Chino aquifer spring samples (fig. E4). In contrast, a single large regional storm on September 15, 2001, produced enough runoff to partially fill Sullivan Lake, with a $\delta^{18}\text{O}$ of -10.4‰ and δD of -76‰ . The stable-isotope ratio for the large rainfall event does not appear to have been affected by evaporation and is 0.4‰ more depleted in $\delta^{18}\text{O}$ than Del Rio Springs. Coincidentally or not, this storm sample is isotopically identical (within laboratory precision) to upper Verde River springs (fig. E4, table E2). While more long-term data are needed to define seasonal variations in $\delta^{18}\text{O}$ and δD in precipitation throughout the study area, it is evident that large regional storms produce less evaporated runoff than small ones and are more likely to generate greater amounts of surface-water runoff and ground-water recharge. No rainfall runoff is known to have topped Sullivan Lake dam for more than 6 months proceeding June, 2000. If Stillman Lake had contained a mixture of ground water and runoff in June 2000, the stable-isotope ratio of the residual runoff would have had to coincidentally fall on the same regression line as the Del Rio Springs and Granite Creek samples. In summary, Stillman Lake water does not appear to have been a mixture at the time of sampling.

As indicated by a statistical summary of stable-isotope data for the sample groups (table E2), the mean $\delta^{18}\text{O}$ value for upper Verde River springs ($-10.3\pm 0.1\text{‰}$) most closely resembles the mean for the four wells penetrating the D-C zone along the basin margin ($-10.4\pm 0.3\text{‰}$). The mean $\delta^{18}\text{O}$ value for the Big Chino sample group (-9.9 ± 0.3) and its range between the maximum of -8.8‰ and minimum of -10.5‰ is misleading, however, in that it does not accurately represent a flow-weighted composite of ground water near the outlet of the basin-fill aquifer, such as at Del Rio Spring or the spring fed reach in lower Williamson Valley Wash. The mean instead represents 35 random well locations that were sampled on different dates from different screened intervals in the upper 700 ft of the aquifer. Upper Verde River springs would seem to represent a flow-weighted composite of Big Chino ground water, however, the possibility of mixing with a small fraction of the M-D sequence along the final leg of the flowpath first must still be ruled out.

In addition, the ^2H and ^{18}O content of shallow ground water beneath Big Chino Wash, Williamson Valley Wash, and near Sullivan Lake is potentially influenced by local recharge and likely enriched relative to the aquifer as a whole. Compelling evidence for direct recharge to the valley floor is based on tritium results presented in the following section.

Consequently, the group mean may be biased. Big Chino well samples near the outlet of the basin-fill aquifer are substantially more depleted in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ than the group mean, and their isotope composition is indistinguishable from that of upper Verde River springs. This helps to explain why the $\delta^{18}\text{O}$ of -10.3‰ for ground water near Paulden (well E at (B-17-02)04 DDC; Appendix B) is isotopically identical to the mean $\delta^{18}\text{O}$ value for upper Verde River springs (table E2), but differs from the group mean.

A $\delta^{18}\text{O}$ value of approximately $-10.3\pm 0.2\text{‰}$ can be used to trace the main flowpath upgradient from upper Verde River springs through the D-C zone to the outlet of the basin-fill aquifer near Paulden. By this approach, no mixing of the Big Chino basin-fill aquifer with another source is required to account for the $\delta^{18}\text{O}$ composition of ground water discharging to upper Verde River springs, within the limits of analytical precision. Trends in water chemistry along this flowpath, including the stable-isotope data, will be further discussed in the final section of this chapter entitled "Multiple Lines of Evidence along a Flowpath."

Figure E5A compares variations in the ^2H and ^{18}O isotopic composition of upper Verde River springs with different geographical regions of the carbonate aquifer, including high-altitude springs on Big Black Mesa, deep wells north of the Verde River near Drake, large springs at Mormon Pocket and Sycamore Canyon, and the D-C zone beneath the margin of the Big Chino basin-fill aquifer. Figure E5B compares samples from upper Verde River springs with those from the two basin-fill aquifers and the high-altitude springs, tributaries, and wells west and south of Big Chino Valley. Most of the samples in the two graphs plot above the WMWL (International Atomic Energy Agency, 1994), suggesting that $\delta^{18}\text{O}$ and δD of local precipitation that is recharged along the Mogollon Rim is more enriched than the global average.

Like the samples from Stillman Lake, the ^2H and ^{18}O isotopic composition of four samples collected from King Spring (Chapter D, fig. D4) between May 2000 and June 2002 have undergone varying degrees of evaporation, as indicated by a slope of approximately 4 (fig. E5A). The dashed blue regression line for the King Spring samples is parallel to the regression line for Stillman Lake, Granite Creek, and Del Rio Spring samples, also with a slope of 4. Left of the WMWL, the King Spring regression line intercepts several other spring samples from the carbonate aquifer near Big Black Mesa. Variation in ^2H and ^{18}O for three samples from Storm Seep, collected on different dates, probably are caused by seasonal variations in evaporation. A sample from Pool Seep plots within $-0.4\pm 0.1\text{‰}$ $\delta^{18}\text{O}$ of the Storm Seep sample, which were both collected on April 19, 2001. Isotopically depleted water at small springs such as Storm Seep and Pool Seep was collected near the point of ground-water discharge, and typically have undergone less evaporation than larger water bodies such as King Spring or Stillman Lake, where the point of ground-water discharge is difficult to detect. The regional water-level gradient (fig. D7, Chapter D, this volume) and the

stable-isotope data indicate that the source of water to King Spring is from the northwest.

Many spring samples and some of the well samples collected during previous studies from stock tanks have undergone evaporation or were not purged prior to sampling, and these samples are not be considered representative of the carbonate aquifer. Two samples from Tucker Canyon and Meath Spring were collected from stagnant pools (fig. E1; Appendix B) and are not included on figure E5A because they are too highly evaporated and plot off scale to the upper right of the graph. Three stable-isotope samples in the carbonate aquifer north of the Verde River are included on figure E5A from previous studies, although the wells apparently were not adequately purged prior to sampling. These include two samples from the Glidden well at B(18-01)27AAC (depth unknown), which were collected from a stock tank by ASU

(Marnie Greenbie, oral commun., 2002), and a sample from the Hell well at B(18-01)06 ABB (depth = 460 ft) which was sampled from a stock tank by the USGS during a previous study (shown on fig. E1; Appendix B; see also Chapter D, this volume, table D3 and fig. D7). In addition, no driller's logs are available for the Hell Well or the Glidden well, making any interpretation uncertain.

The two Glidden well samples are within 2-sigma analytical precision of the $\delta^{18}\text{O}$ analyses for upper Verde River springs (table E2; Appendix B), leading to Knauth and Greenbie's (1997) interpretation that the source of upper Verde River springs is the carbonate aquifer north of the upper Verde River. The two δD values, however, fall off the WMWL and are isotopically different from those for upper Verde River springs, although if averaged together they would produce a value nearly identical to upper Verde River springs. No explanation

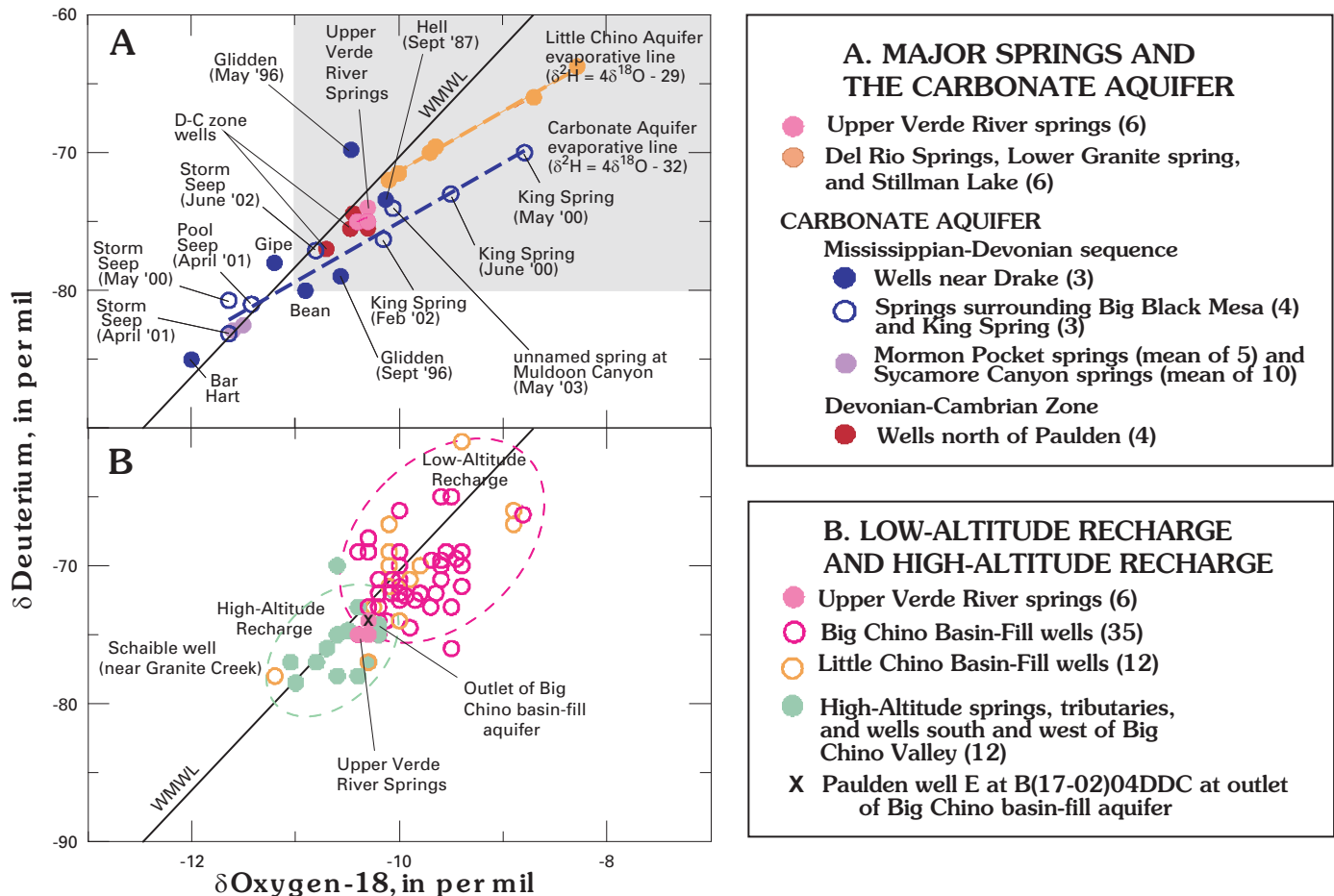


Figure E5. Graphs showing δD versus $\delta^{18}\text{O}$ for sample groups in the Verde River headwaters (1986–2004); (A) major springs discharging to the upper Verde River versus wells and springs in the carbonate aquifer, and (B) upper Verde River springs versus Big and Little Chino basin-fill aquifers and high-altitude springs, tributaries and wells. In graph A, all analyses were used to illustrate seasonal variability of evaporative trends for surface water. In the graph B, in cases where multiple analyses were available for a single well location, the median values were used to minimize sample distribution bias. All data are reported in Appendix B. Shaded area in upper graph represents the graph area shown in figure E4. Number in parentheses in the explanation is number of samples in group. WMLW = World Meteoric Water Line ($\delta\text{D} = 8\delta^{18}\text{O} \pm 10$).

is made here for the large disparity between the two δD values with the $\delta^{18}O$ values essentially remaining constant. Compared with the new data from this study, the stable-isotope signature of the Glidden sample collected in September 1996 more closely resembles that of the Gipe and Bean samples than that for upper Verde River springs. The Glidden sample collected in May 1996 plots above the WMWL, and is different than all the other samples. Because of the differences in the δD values, a lack of other lines of geochemical evidence, and the absence of a well log, interpretation of the Glidden well is considered inconclusive.

Samples in the carbonate aquifer which have not undergone substantial evaporation include three wells north of the upper Verde River (Bean, Gipe, and Bar Hart wells shown on figs. E1 and E5A) and large low-altitude springs at Sycamore Canyon and Mormon Pocket. The wells range in depth from 585 to 720 ft and all three were pumped extensively before sampling. The Sycamore Canyon and Mormon Pocket springs, with steady discharge exceeding $5\text{ft}^3/\text{s}$, have been sampled repeatedly with little variation. All these M-D sequence samples are more depleted than upper Verde River springs (on average 1.3‰, table E2) plotting near or left of the WMWL. Thus, the M-D sequence of this part of the carbonate aquifer is substantially depleted in ^2H and ^{18}O compared to upper Verde River springs and based on water-level gradients could not contribute to the upper Verde River upstream from Perkinsville (Chapter D, this volume). Likely sources of recharge near Drake include direct recharge of runoff along Limestone Canyon and Hell Canyon, which are deeply incised to just above the water table in some reaches. The evident source of recharge to springs at Mormon Pocket and Sycamore Canyon is the extensive high-altitude region surrounding Bill Williams Mountain to the north (Wirt, 1993; Bryson and others, 2004).

Well samples from the two basin-fill aquifers plotted on fig. E5B show a broad scatter pattern of stable-isotope ratios. Samples from the Big Chino basin-fill aquifer (open pink circles) plot to the upper right of upper Verde River springs (solid pink circles), a pattern overlapping with and similar to the pattern of samples for the Little Chino basin-fill aquifer and Little Chino low-altitude springs (orange open and solid circles, respectively). Both Big and Little Chino basin samples generally are enriched in $\delta^{18}O$ and δD compared to upper Verde River springs—a trend attributed to a higher fraction of recharge at lower altitudes derived from losing tributary streams and seepage beneath ephemeral streams. In contrast, high-altitude samples from springs in the Bradshaw, Santa Maria, and Juniper Mountains (elevations $> 4,500$ ft) and major tributaries including Williamson Valley Wash and Walnut Creek (solid green circles) are substantially more depleted and plot in a scatter pattern overlapping with and to the lower left of upper Verde River springs. High-elevation samples represent ground water that is recharging the edges of the basins. An exception is a highly-depleted sample from the Schaible well in Little Chino Valley (figs. E1 and E5B; B-16-01 17 CCB), which plots similarly to the high-altitude well

and spring samples. The well is less than $\frac{1}{4}$ mi from Granite Creek and probably receives direct recharge from high-altitude runoff during exceptionally large but infrequent storms.

Thus, two types of recharge appear to be occurring within the study area. High-altitude recharge is depleted relative to upper Verde River springs, owing to greater precipitation and cooler temperatures (Chapter A, this volume; fig. A9 and table A2). Low-altitude recharge to the basins is enriched relative to upper Verde River springs, owing to warmer temperatures and evaporation of overland flow on the valley bottoms. Ground water near the outlets of the Big and Little Chino basin-fill aquifers is a volumetric composite of both types of recharge. Samples from upper Verde River springs, the four D-C zone well samples, and basin-fill well E at (B-17-02)04 DDC near Paulden plot between the two oval-shaped scatter patterns for the basin-fill aquifers and high-altitude area samples (fig. E5B), as would be expected for a composite of high- and low-altitude recharge.

At the risk of redundancy, we reiterate that an important limitation of the stable-isotope data used in this study is not being able to volumetrically weight contributions from various parts of the ground-water system. As mentioned previously, most of the ground-water samples were collected from springs and wells that are less than 700 ft in depth. The basin-fill aquifer in Big Chino Valley is at least 2,000 ft deep in the center of the basin (Langenheim and others, Chapter C, this volume). Deep ground water in the centers of large basins is likely to have been recharged during a cooler and wetter climatic period (Robertson, 1991) or may be comprised of mostly high-altitude recharge. Deep ground water, which is largely unsampled, is expected to be more depleted in $\delta^{18}O$ and δD than the relatively shallow well water sampled in this study. Deep ground water eventually must flow toward the outlet of the basin-fill aquifer. The hypothesis that mixing occurs between the basin-fill aquifer and underlying carbonate aquifer as deep and shallow flowpaths converge near the outlet will be evaluated by inverse modeling in Chapter F (this volume).

The range in $\delta^{18}O$ data for each sample group has been summarized using box- and whisker plots (fig. E6). The box- and whisker plots for upper Verde River springs and the D-C zone of the carbonate aquifer underlying Big Chino Valley are nearly identical, suggesting that the two ground waters have a similar source. The $\delta^{18}O$ box- and whisker plots for upper Verde River springs and the D-C zone are more depleted than that for the Big Chino basin-fill aquifer sample group, but closely match the sample from well E at (B-17-02)04 DDC, which is representative of ground water at the outlet of the Big Chino basin-fill aquifer near Paulden.

Wells between Paulden in the basin-fill aquifer and upper Verde River springs in the D-C zone have similar $\delta^{18}O$ content because they essentially lie along the same flowpath. Water-level gradients indicate the direction of ground-water movement near Paulden is east, from the basin-fill aquifer into the carbonate aquifer and then southeast toward the upper Verde River (Chapter D, this volume, fig. D7). Large well yields

in wells penetrating limestone is an indication of solution features and preferential flow along the extension of the Big Chino Fault trend and basin-fill aquifer boundary (Chapter D, this volume). Secondary fractures and joint sets in basalt and Paleozoic sedimentary rocks provide yet another conduit out of the basin-fill aquifer.

The stable-isotope data do not convincingly indicate that upper Verde River springs is a mixture of two sources, unless both sources have fairly similar $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopic composition, or unless the contribution from one source is relatively minor. On average, the carbonate aquifer north of the Verde River (M-D sequence) typically is 1.3‰ more depleted in $\delta^{18}\text{O}$ than upper Verde River springs (table E2), or—particularly in the case of the Glidden and Hell wells, and the King Spring samples—so enriched by evaporation

or having sampling uncertainties such that no conclusive interpretation can be made. Based on the regional water-level gradients, some mixing with the carbonate aquifer could occur west or north of upper Verde River springs (Chapter D, this volume; figs. D6 and D7). Using a mass-balance approach, the maximum hypothetical contribution from the M-D sequence of the carbonate aquifer north of the Verde River that could occur, without affecting the $\delta^{18}\text{O}$ content of upper Verde River springs by more than 0.2‰ (the analytical precision of the technique), is about 15 percent. Ford (2002) estimated recharge from the carbonate aquifer underlying Big Black Mesa at about 5 percent of the base flow to the upper Verde River (Chapter A, this volume; fig. A16 and table A4). A 5-percent mix with the carbonate aquifer would be too small to produce a statistically significant shift in the

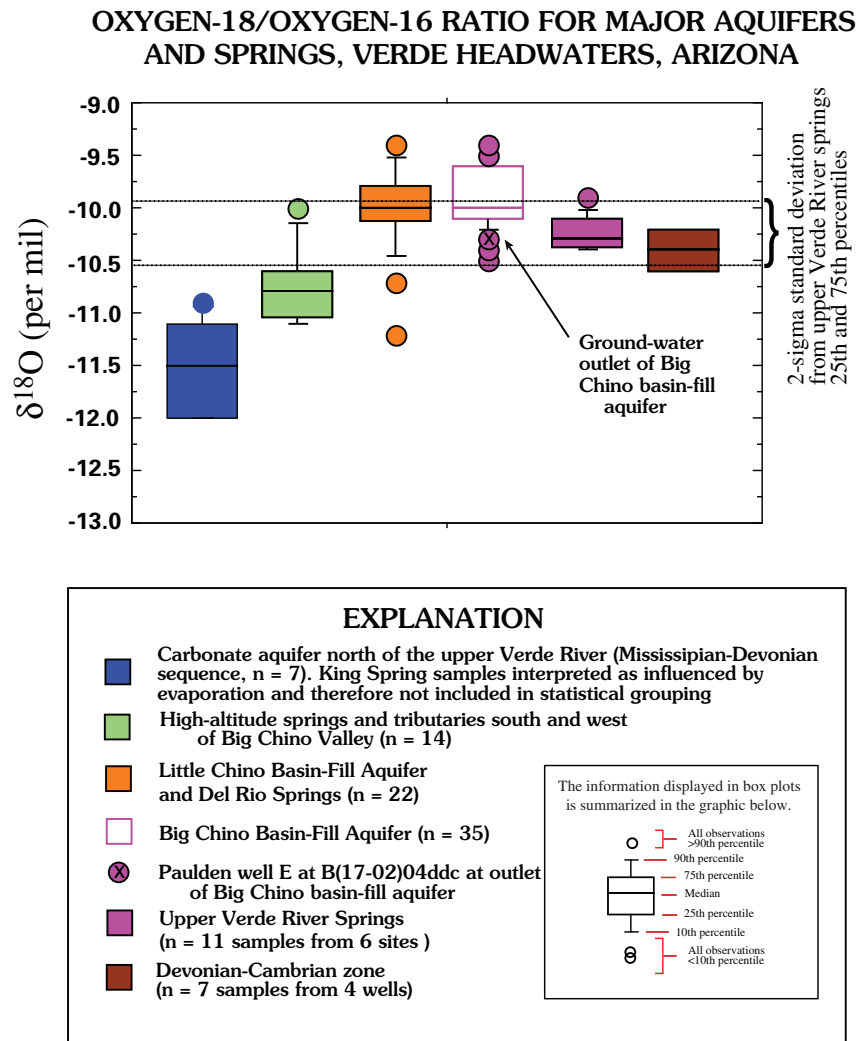


Figure E6. Box- and whisker plot (SAS Institute, 1998) of $\delta^{18}\text{O}$ for sample groups upgradient of upper Verde River springs. Order of box- and whisker plots is the same as in explanation; n, is number of samples. Data are summarized in table E2.

$\delta^2\text{H}$ and $\delta^{18}\text{O}$ composition. Thus, no indisputable conclusion can be reached based on stable-isotope evidence alone except that the amount of mixing, if any, is less than about 15 percent. The mixing hypothesis will be further evaluated by inverse geochemical modeling in the following chapter (Chapter F, this volume).

Apparent Age of Ground Water

Tritium and ^{14}C data provide a useful means of estimating apparent age and degree of mixing and for delineating ground-water movement. Spatial differences in the activities of tritium and ^{14}C on figs. E7 and E8 illustrate flowpath directions and areas where recharge is occurring. Detectable tritium values are interpreted to mean that the water is either modern in age, or contains a fraction of modern water. Ground water having a low ^{14}C activity, expressed as percent modern carbon (pmc), is presumed older than waters having a higher percentage of modern carbon. Ground-water ages have not been calculated for this study.

Tritium

Tritium activities in ground water (fig. E7) are interpreted relative to modern local precipitation. Two precipitation samples in the study area were analyzed for tritium during the summer of 2001. A composite of summer rain collected from roof runoff by a local resident of Chino Valley contained 9.1 ± 0.41 tritium units (TU). The composite sample was collected by transferring runoff into a large sealed container immediately following each storm. In no instance did the roof runoff exceed the capacity of the collection container. A large regional storm on September 15, 2001, contained 5.0 ± 0.36 TU. Both activities are consistent with background values for modern precipitation in southern Arizona ranging from about 5 to 10 TU (Christopher J. Eastoe, oral commun., 2004; Wright, 2001). The highest tritium values in the study area are samples from high-altitude springs on Big Black Mesa and in the Bradshaw, Santa Maria, and Juniper Mountains; ranging from 3.1 to 10.3 tritium units (mean = 6.4 ± 3.6 TU; $n = 11$). None of the samples appear to contain high levels of bomb-pulse tritium leftover from the 1950s and 1960s, suggesting that all of the water has been recharged since 1953. Samples from alluvial aquifers along major tributaries have less tritium activity and appear to be older relative to high-altitude springs. In Walnut Creek, a sample from a 150-ft well had a value of <0.7 TU, and in Williamson Valley a 190-ft well and a spring sample had values of 1.3 and 3.8 TU, respectively. The age of the water in the Walnut Creek sample probably is pre-1953; whereas the two Williamson Valley sample values contain at least a fraction of water recharged since 1953.

Ground water from three wells in the northwestern Big Chino basin-fill aquifer (wells A, B, and C) had no detectable tritium, as did well H in the D-C zone of the carbonate aquifer north of Paulden. Two wells near Sullivan Lake (wells E and F) and one well near the confluence of Big Chino Wash with Williamson Valley (well D) had 1.2, 1.2, and 1.1 TU of

detectable tritium. Low levels of tritium suggest that direct recharge to the basin-fill aquifers is occurring along low-altitude ephemeral reaches. The largest tritium value of 2.7 ± 0.3 TU measured for well L in the Little Chino basin-fill aquifer is from a 350-ft well in the Granite Creek flood plain. This sample also is heavily depleted in $\delta^{18}\text{O}$ and δD (fig. E5), which is a further indication that high-altitude runoff has infiltrated beneath the ephemeral reach of Granite Creek.

Low levels of tritium detected in springs near the outlets of the basin-fill aquifers indicate recharge of intermittent storm runoff. Along the uppermost reach of the Verde River, tritium activities ranged from <0.5 to 2.3 TU (Appendix B). At Paulden, north of Sullivan Lake and near the outlet for the Big Chino basin-fill aquifer, a sample from a basalt well B(17-02)02 CAC had a tritium activity of 0.8 TU, just above the reported detection level for that sample. This well is along the main flowpath between Paulden and upper Verde River springs, as indicated by water-level gradients presented by Wirt and DeWitt (Chapter D, this volume). Tritium values for seven different samples from upper Verde River springs collected during May–June 2000 ranged from <0.7 to 1.1 TU. During the same time, five samples from Lower Granite Spring and Del Rio Springs had values ranging from 0.9 to 1.6 TU. Following extended drought conditions, two samples at Stillman Lake had <0.7 TU in May and June of 2000. After a large regional storm in September 2001, Stillman Lake had a tritium activity of 2.3 ± 0.6 TU on January 16, 2002. Similarly, Summer Spring in Sycamore Canyon at stream level had a low but detectable value of 1.1 ± 0.3 TU. The large spring at Mormon Pocket had <0.6 TU. This spring discharges above all but the highest floods in this reach.

In summary, water from high-altitude springs and major tributaries had the highest tritium activities and youngest apparent ages. None of the tritium values exceed 10 TU, a level that would indicate that some portion of precipitation was recharged during atmospheric nuclear testing of the 1950s and 1960s, or post fallout during the 1970s. Samples from wells greater in depth than 500 ft in northwestern Big Chino Valley and from the carbonate aquifer had no detectable tritium, indicating that ground water was recharged before 1953. The presence of low-level tritium in springs and wells near streams indicates that modern direct recharge is occurring along Williamson Valley Wash, southeastern Big Chino Wash, middle and lower Granite Creek, and in the areas near Sullivan and Stillman Lakes. Major springs near the outlets of Big and Little Chino Valleys tend to have tritium activities slightly above the analytical detection limit, which is consistent with low-altitude recharge occurring along low-gradient stream segments.

Carbon-14 and Carbon-13

Carbon-14 was analyzed for samples from fourteen wells and low-altitude springs. Because high-altitude springs represent modern recharge, as indicated by elevated tritium activities, none of these samples were further analyzed for ^{14}C .

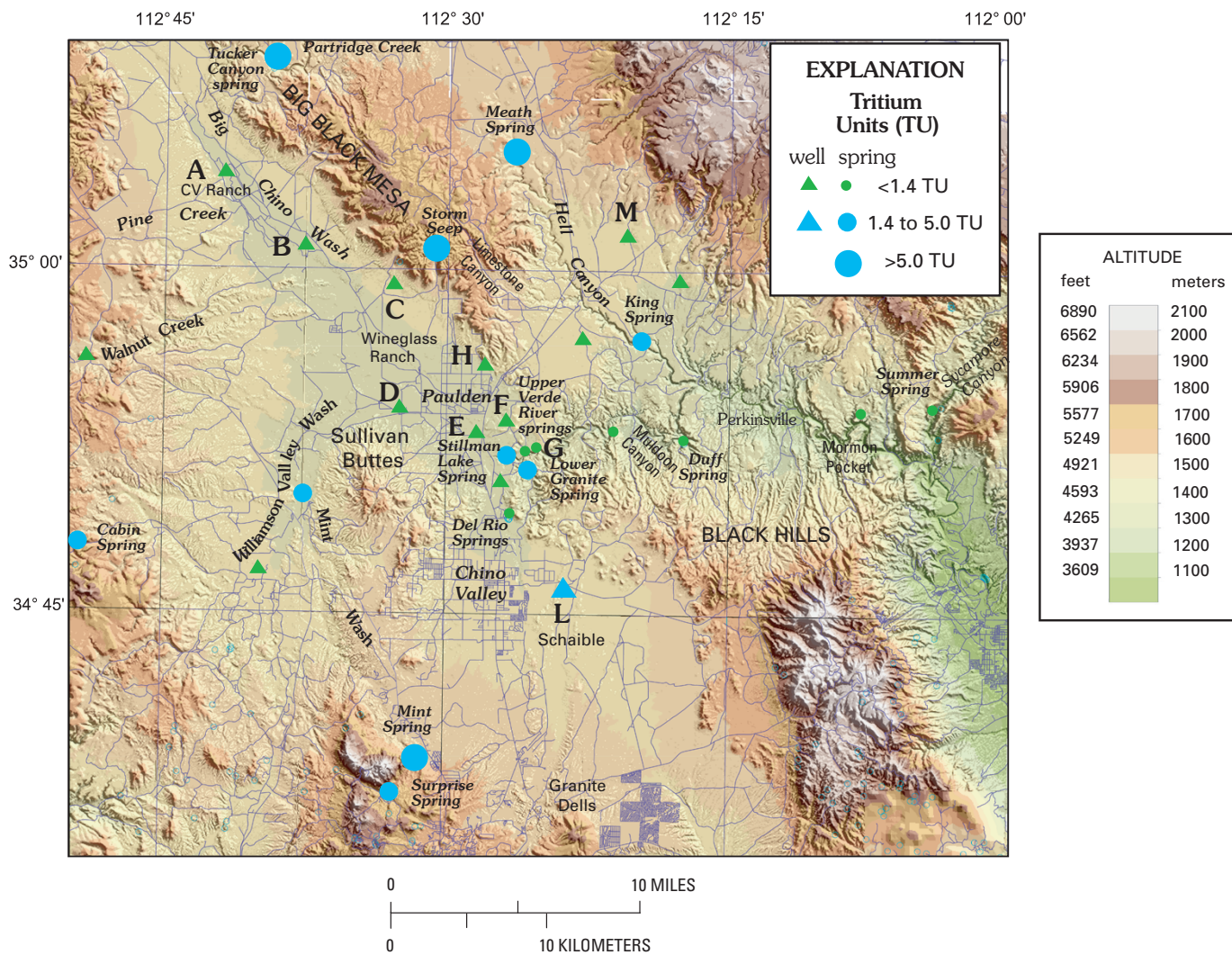


Figure E7. Map showing tritium activities measured in this study, upper Verde River headwaters region. Base is from 1:100,000 U.S. Geological Survey digital data. Circle is spring sample, triangle is well sample. Lettered location corresponds to samples plotted in graphs on figure E9. Data are reported in Appendix B.

The highest ^{14}C activities > 65 percent modern carbona (pmc), indicative of younger ground water, are found along major tributaries adjacent to high-altitude recharge areas receiving the most precipitation (fig. E8). A sample from a 150-ft well in Walnut Creek contained 81.1 ± 0.6 percent modern carbon (pmc) and a 190-ft well and spring in Williamson Valley Wash contained 79.1 ± 0.7 and 106.5 ± 0.8 pmc, respectively. The latter ^{14}C value exceeding 100 pmc is similar to that measured for air in southern Arizona in 2002 (Eastoe and others, 2004).

Carbon-13 for the entire study area ranged from -1.9 to -15.2‰ (average = -8.6 ; $n = 45$). As mentioned in the methods section, the primary source of $\delta^{13}\text{C}$ in ground water is CO_2 in the soil gas of the recharge zone (Bullen and Kendall, 1998). The lowest $\delta^{13}\text{C}$ values generally were measured from springs in riparian areas and from well samples having detectable tritium and also having among the highest ^{14}C activity. All

three samples from Williamson Valley and Walnut Creek had > 75 pmc ^{14}C and moderately depleted $\delta^{13}\text{C}$ of -11.2 , -11.9 and -12.2‰ , respectively.

Other high ^{14}C activities were measured for the 350-ft well in the Granite Creek flood plain in Little Chino Valley (73 pmc; $\delta^{13}\text{C} = -7.9$) and a 250-ft well south of Sullivan Lake (87 pmc; $\delta^{13}\text{C} = -11.7$). Ground water from the Little Chino basin-fill aquifer is progressively younger toward the Verde River, as evidenced by ^{14}C activities of 66, 81, and 97 pmc for Del Rio Springs, Lower Granite Spring, and Stillman Lake, respectively. This increasing trend is evidence of direct recharge of runoff to ground water beneath low-gradient stream channels, consistent with the results for the tritium data.

The lowest ^{14}C activities indicating the oldest water were measured from well samples having no detectable tritium and relatively enriched $\delta^{13}\text{C}$. Five samples from the

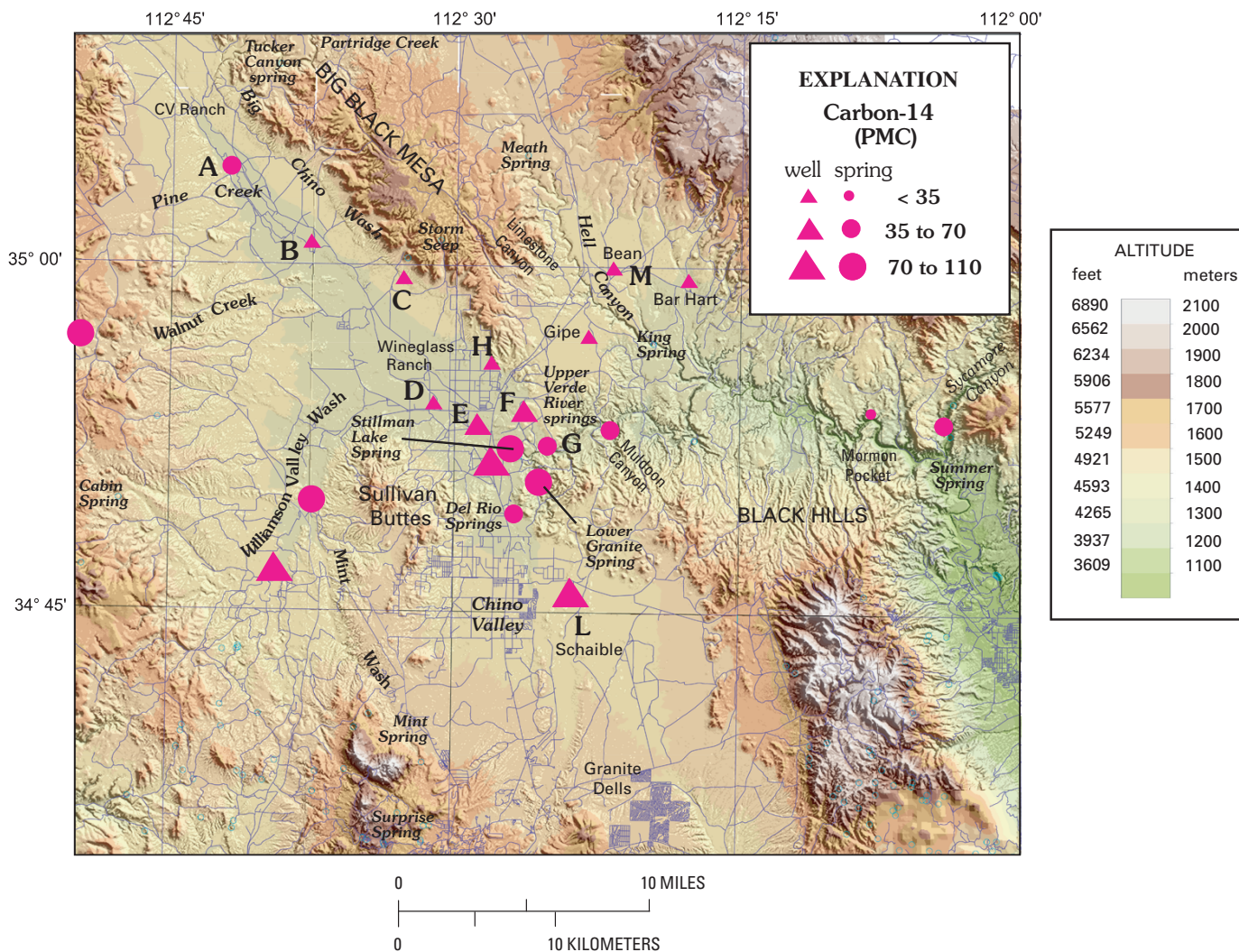
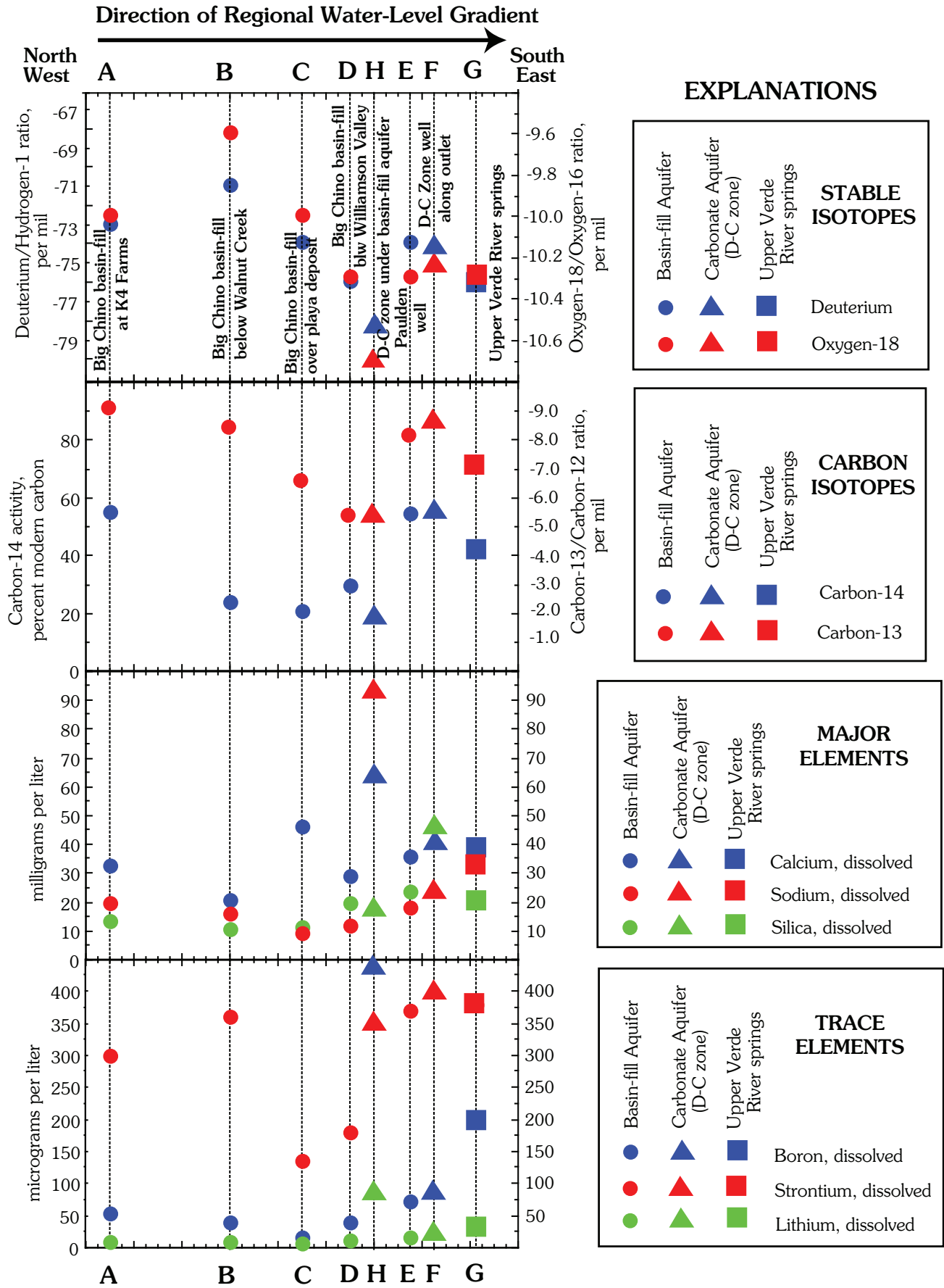


Figure E8. Map showing carbon-14 activities measured in this study, upper Verde River headwaters region. Base is from 1:100,000 U.S. Geological Survey digital data. PMC, percent modern carbon; circle is spring sample, triangle is well sample. Lettered location corresponds to samples plotted in graphs on figure E9. Data are reported in Appendix B.

carbonate aquifer north of the Verde River had values of 18.6 to 36.4 pmc and -7.7 to -2.0 $\delta^{13}\text{C}$ ($\delta^{13}\text{C}$ average = -6.0 ± 2.3 ; $n=5$). Ground water with a similar range of ^{14}C activity was measured for two out of six wells sampled in Big Chino Valley. The lowest measured ^{14}C activity of 18.0 ± 0.2 pmc was measured for a sample from well H north of Paulden ($\delta^{13}\text{C} = -5.6$; figs. E8 and E9), which was completed in the carbonate aquifer underlying the Big Chino basin-fill aquifer. The 346-ft well is near the terminus of the Big Chino Fault and was drilled through alluvial fan sediment into what is interpreted as the D-C zone of the carbonate aquifer. A second low value of 21.0 ± 0.2 pmc and -6.7% $\delta^{13}\text{C}$ was measured for a 190-ft well (site C) completed in alluvial fan sediment near the Big Chino Fault at the base of Big Black Mesa. One explanation for the two samples essentially having the same ^{14}C activity is that they could be along a similar flowpath roughly

parallel to the Big Chino Fault. A second possible explanation is that, in both cases, the local ground water is in contact with carbonate rock or carbonate sediments and that the dissolution of carbonate minerals has contributed “dead” carbon to the ground water. Thus, it is unclear whether the ground water is really old or whether there has been an addition of dead carbon resulting in values that appear older. Geochemical modeling is needed to correct for the presence of dead carbon and to calculate numerical ages for the ground water samples.

If the Big Chino basin-fill aquifer were a closed aquifer system, one would expect ground water to appear progressively older along the valley axis from northwest to southeast. But because the aquifer is an open system, ground water changes in age in relation to depth and distance from recharge sources such as Big Chino Wash and



its major tributary streams. The apparent age of ground water in the basin-fill aquifer varies not only along the axis of the basin, but in relation to many factors such as the distance from recharge sources, rates of ground-water movement, changes in the lithology of water-bearing units, and the depth of the well screen. Sampling limitations make it impossible to determine a possible relation between water chemistry and depth. In addition, no wells were sampled across the wide confluence of Williamson Valley with Big Chino Valley.

In northwestern Big Chino Valley, ^{14}C activity decreases along the axis of the upper basin from 55.0 ± 0.6 to 24.1 ± 0.5 pmc between Partridge Creek and Walnut Creek (between well A and well B shown on figs. E8 and E9). Near the center of the basin, one might predict that relatively younger water from Walnut Creek and Williamson Valley Wash would enter and mix with the Big Chino basin-fill aquifer and that the next sample along the axis of the basin should be younger. In fact, the value of 29.8 ± 0.6 pmc for well D north of Sullivan Buttes in Quaternary and Tertiary alluvium is only slightly higher, or younger than the sample upgradient from Walnut Creek. That the value is not substantially higher (indicating apparently younger water) may be because the thickness of the aquifer decreases along its axis from at least 2,000 ft in the deepest part of the basin to several hundred ft or less in the southeastern part of the valley (Langenheim and others, Chapter C, this volume). Deeper circulating ground water may migrate upward along preferential flowpaths, particularly along fault-bounded margins on the north and south sides of the basin. This hypothesis would explain the relatively lower ^{14}C activity for wells D and H and also might explain in part why many productive wells have been developed in lower Big Chino Valley near the distal end of the aquifer. East of Wineglass Ranch, yields exceeding 1,000 gallons per minute have been reported for wells completed in basin-fill alluvium, in basin-fill basalt, and in the carbonate aquifer underlying the basin-fill aquifer (Water Resources Associates, 1989; 1990; Chapter D, this volume). All of these aquifer units are thought to be hydraulically connected.

The hydrogeologic framework for southeastern Big Chino Valley is briefly summarized here from Chapter D (Wirt and DeWitt, this volume) for the area downgradient from Wineglass Ranch. Ground water from Williamson Valley merges with the Big Chino basin-fill aquifer near Wineglass Ranch. As ground water moves down the axis of Big Chino Valley toward the main ground-water outlet near Paulden, it encounters buried basalt flows within the alluvium. The buried

basalt is 500 ft in depth with a thickness of 90 ft in a borehole west of Wineglass Ranch (DeWitt and others, Chapter B, this volume). The basalt exposed at Sullivan Lake is about 350 ft thick. The water-level gradient of the Big Chino basin-fill aquifer near Paulden slopes gently east or southeast, toward upper Verde River springs, the main point of discharge for the Big Chino aquifer (Chapter D, this volume). The Big Chino basin-fill aquifer and the D-C zone are strongly interconnected in this part of the basin as shown by a dashed basin-fill aquifer boundary east of Paulden (fig. E1). This interpretation is supported by a gently-sloping water-level gradient that extends over a broad area from Paulden on the west, to upper Verde River springs and the Verde River on the south, to King Spring on the east, and at least 2.0 mi north of Drake (Chapter D, fig. D7). Ground water leaving Big Chino Valley near Paulden travels approximately 1.5 mi through the carbonate aquifer (which includes a basalt paleochannel) before reaching upper Verde River springs.

The main flowpath between Paulden and upper Verde River springs is indicated by the lack of change in ^{14}C activity and $\delta^{13}\text{C}$ ratio for wells E and F (fig. E8) that is consistent with the water-level gradient. Well E near Paulden (at B-17-02 04 DDC) is 200 ft in depth and produces from the basin-fill aquifer. Well F is 1.5 mi north of upper Verde River springs (site G), 480-ft deep, and produces from the carbonate aquifer just east of the Big Chino basin boundary. Both wells E and F penetrate the same correlated basalt units, are less than 1.5 mi apart, and have essentially the same ^{14}C activity (54.7 ± 0.8 versus 55.5 ± 0.6 pmc) and $\delta^{13}\text{C}$ ratio (-8.2 versus -8.8%). Continuing along the flowpath, ground water discharging to the main spring G in the upper Verde River springs network has a ^{14}C activity of 42 ± 0.3 pmc (-7.0% $\delta^{13}\text{C}$). The slightly lower ^{14}C value may be due in part from dissolution of dead carbon from carbonate rocks along the final leg of the flowpath. Alternately, mixing with a small amount of apparently older ground water such as that for well H in the D-C zone north of Paulden, with a ^{14}C activity of 18.0 ± 0.3 pmc and -5.6% $\delta^{13}\text{C}$, would also account for the slight decrease in ^{14}C activity and $\delta^{13}\text{C}$ content at upper Verde River springs. Mixing versus water-rock interaction processes are further addressed in the following section and in Chapter F (this volume).

Multiple Lines of Geochemical Evidence along a Flowpath

Stable-isotopes alone do not always uniquely identify water sources. Where more than one interpretation is possible, knowledge of water-level gradients, geological factors, and other geochemical evidence can help to rule out unlikely scenarios. The most likely scenario can be identified when all chemical and isotopic data are considered in their geologic and hydrologic context. Water-chemistry and isotope data presented in this chapter have been used to characterize the basin-fill aquifers, stratigraphic units and geographical areas within

Figure E9 (facing page). Graphs showing changes in water chemistry along regional water-level gradient from upper to lower Big Chino Valley and from the Big Chino basin-fill aquifer near Paulden through the carbonate aquifer to upper Verde River springs. Letter on x-axis corresponds to sample location shown in figure E8. Horizontal spacing is proportional to map distance.

the carbonate aquifer, high-altitude recharge areas, and major springs discharging to the upper Verde River and its tributaries. Chemical and isotopic data provide integrated information for ground water discharging from the major aquifers. Different geochemical constituents help to constrain hypotheses regarding the nature of water-rock interactions and possible end-members involved in mixing processes.

To summarize the different lines of geochemical evidence presented thus far in this chapter, upper Verde River springs and Little Chino basin-fill aquifer are easily distinguished from each other on the basis of trace-element concentrations and stable-isotope ratios. Del Rio Springs and Lower Granite Spring are $\sim 0.4\%$ heavier in $\delta^{18}\text{O}$, and have strontium concentrations exceeding $450\ \mu\text{g/L}$ compared with moderate Sr (346 to $440\ \mu\text{g/L}$) for upper Verde River springs. Ground-water discharge from the Little Chino basin-fill aquifer has more contact with Sr-rich volcanic rocks and less exposure to sedimentary rocks in the D-C zone. In contrast, upper Verde River springs contain moderately high concentrations of 17 – $29\ \mu\text{g/L}$ As, 136 – $270\ \mu\text{g/L}$ B, and 28 – $49\ \mu\text{g/L}$ Li. This compares with 7 – $17\ \mu\text{g/L}$ As, 40 – $80\ \mu\text{g/L}$ B, and 7 – $17\ \mu\text{g/L}$ Li for samples from Del Rio Springs, lower Granite Creek, and Stillman Lake.

Ground water from upper Verde River springs and the M-D sequence also are easily distinguished from one another. The isotope composition of upper Verde River springs is enriched by about 1.3% and 7.9% in $\delta^{18}\text{O}$ and δD relative to the M-D sequence north of the Verde River (fig. E6; table E2). The M-D sequence also has relatively low levels of trace-elements (101 – $120\ \mu\text{g/L}$ Sr, 2 – $10\ \mu\text{g/L}$ As, 12 – $71\ \mu\text{g/L}$ B, and 3 – $15\ \mu\text{g/L}$ Li; fig. E3); however, these elements could be acquired later through contact with the D-C zone. A substantial contribution from the M-D sequence of the carbonate aquifer would be expected to deplete the $\delta^{18}\text{O}$ of upper Verde River springs, but this argument is not compelling given the degree of variation in the data. A small amount of mixing, within the margin of analytical uncertainty for the $\delta^{18}\text{O}$, cannot be ruled out with a simple mass-balance approach. The M-D sequence could provide up to about 15 percent of the total discharge to upper Verde River springs without changing the $\delta^{18}\text{O}$ by more than 0.2% . Recharge from Big Black Mesa has been estimated at about 5 percent of base flow at the Paulden gauge, based on its aerial extent and rate of precipitation (Ford, 2002; Chapter A, this volume; fig. A16). A mixing contribution on this scale could not be confirmed or rejected by the stable-isotope evidence alone and therefore this hypothesis will be further tested by inverse geochemical modeling at the end of the following chapter (Chapter F, this volume). Trends in major and trace-element concentrations presented here indicate that water-rock interaction, as opposed to mixing with the M-D sequence, is the major process occurring along the Big Chino outlet flowpath.

A conceptual summary of water chemistry along the main ground-water flowpath—down the axis of northwestern Big Chino Valley to southeastern Big Chino Valley, and from the Big Chino basin-fill aquifer through the carbonate aquifer

to upper Verde River springs—is presented on fig. E9 (sample locations shown on fig. E8). Samples A and B were collected from deep irrigation wells in the Big Chino basin-fill aquifer upgradient of Walnut Creek. Samples from wells C and D were collected near the northern and southern margins of the central basin, respectively. Preferential flow out of the basin-fill aquifer is thought to occur along a flowpath from wells E, to F, to G. The basin-fill aquifer at E predominantly consists of buried basalt layers at Paulden. Sample F also penetrates basalt within the carbonate aquifer east of Paulden. Sample G is the largest spring in the upper Verde River springs network. Sample H is from the area along the Big Chino Fault and represents water that has had extensive contact with the D-C zone.

In the uppermost graph, $\delta^{18}\text{O}$ and δD ratios initially increase and then become more depleted with distance along the conceptual flowpath down the axis of Big Chino Valley. East of Wineglass Ranch, the $\delta^{18}\text{O}$ and δD values for well samples D, E, and F are within analytical precision of upper Verde River springs (G), suggesting a major flowpath that approximately follows this route. The $\delta^{18}\text{O}$ and δD at the outlet of the Big Chino aquifer (sample E on fig. E9) closely matches well F and upper Verde River springs (G). Samples F and H are within the D-C zone along the outlet flowpath but differ slightly to within 0.4% $\delta^{18}\text{O}$ and 4.0% δD (2-sigma analytical uncertainty) of upper Verde River springs. The mean stable-isotope ratio for nine samples from upper Verde River springs, however, closely match that for five samples from the D-C zone within 0.1% $\delta^{18}\text{O}$, which is within 1-sigma analytical uncertainty of 0.2% (table E2). Sample H is the most depleted in $\delta^{18}\text{O}$ and δD of all the samples from the D-C zone (fig. E6). Consequently, a small amount of mixing of the D-C zone with the Big Chino basin-fill aquifer—even if one were to use the most depleted result—would not produce a significant shift in the stable isotope composition of upper Verde River springs.

In the second graph (fig. E9), ^{14}C activities decrease along the valley axis from samples A to C, then increase from D to F. The increase in modern ^{14}C toward the basin outlet corresponds with the increase in measurable tritium activity (fig. E7), indicating that direct recharge from infrequent runoff probably is occurring along Big Chino Wash, lower Williamson Valley Wash, and near Sullivan Lake. A slightly lower ^{14}C activity at upper Verde River springs (G) might be caused by mixing with older deeper water near the outlet for the basin-fill aquifer, or by dissolution of carbonate rocks contributing ‘dead’ carbon, if this process were occurring. A proportionate decrease in $\delta^{13}\text{C}$ from -8.8 to -7.0% from samples E and F to G corresponds with the lithology change along the flowpath from basalt to limestone and suggests that a small amount of mixing or dissolution of carbonate rocks is occurring.

The third graph (fig. E9) shows concentrations of dissolved calcium, sodium, and silica (as Si). Dissolution of calcite and dolomite in the carbonate aquifer would be expected to calcium concentrations from well E to spring G; yet the concentrations remain nearly constant along this flowpath. Using NETPATH (Plummer and others, 1994), saturation

indices for calcite of -0.78 and -0.37 were calculated for two samples from upper Verde River springs (spring G or SP1700). This indicates that the ground water is near saturation or slightly undersaturated with respect to calcite. Cation exchange with clay minerals, common in shale (Potter and others, 1980), also might account for the lack of change in Ca concentration, which is accompanied by an increase in Na concentration from well E to spring G. Mixing or contact in the D-C zone (represented by well H) results in a Ca concentration about one third higher and a Na concentration 6 times higher than the concentrations at upper Verde River springs (spring G). In addition, dissolved silica is slightly higher near Paulden than the rest of big Chino Valley, but is about twice as high at well F, which intercepts the basalt paleochannel. This is consistent with dissolution of silicate minerals in igneous rock. Disproportionate changes in major ion concentrations (or lack thereof) are more likely caused by water-rock interaction and are difficult to explain solely by mixing.

In contrast to Ca and Si, concentrations of Na, B, and Li increase from well D to spring G, also presumably the result of water-rock interactions. Between well E and spring G there are 189 and 188 percent increases in the concentrations of Na and Li, respectively (probably the result of a correlated dissolution processes). Boron increases from well D to spring G by 274 percent, likely caused by a different process or solid-phase distribution. Both B and Li sorb weakly and tend to remain in the dissolved state (Hem, 1985); hence these disproportionate changes in the concentrations of these constituents are best explained by water-rock interaction as opposed to mixing. This observation is reinforced by the lack of significant change in $\delta^{18}\text{O}$ and δD values along the same flowpath (well D to spring G). Stable-isotope ratios of oxygen and hydrogen are the parameters most likely to behave conservatively (fig. E9) and these also support the interpretation that little mixing is occurring (within the analytical precision of the technique).

Lastly, elevated Sr concentrations are most strongly linked to volcanic rocks, although a playa source is possible for some wells in middle and lower Big Chino Valley. Strontium concentrations are moderately high in the northwest and southeast parts of the Big Chino basin-fill aquifer, where there is spatial proximity downgradient from buried basalt flows (wells A, B, and E). Strontium concentrations are lowest for wells C and D near the northern and southern basin margins where there is no contact with the playa deposit or buried basalt. Strontium concentrations are similar for the Big Chino basin-fill aquifer near its outlet (well E) and the D-C zone (F and H), suggesting that a playa or igneous source of Sr is upgradient from the D-C zone. Basalt-filled paleochannels may also provide an additional source of strontium to well F and spring G. Conversely, mixing of ground water from the low-Sr M-D sequence with ground water traveling through the D-C zone would be expected to produce a lower Sr concentration at spring G. This does not appear to be the case and there again is a lack of geochemical evidence to support mixing.

In conclusion, the results of the geochemistry investigation reinforce the hydrogeologic framework conceptual model that the Big Chino basin-fill aquifer and underlying carbonate aquifer are strongly interconnected along the basin outlet flowpath near Paulden and appear to function as a single source of ground water to upper Verde River springs. Overall, the results from this geochemical study indicate considerable vertical and horizontal heterogeneity of the Big Chino basin-fill aquifer and its underlying carbonate aquifer that need to be considered when establishing a regional ground-water model. Paleozoic rocks are presumed to underlie all or most of Big Chino Valley, although there are no ground-water samples from the lower carbonate aquifer except for those from the D-C zone north of Paulden along the trend of the Big Chino Fault. Overall similarities among the stable-isotope ratios measured for the Big Chino basin-fill aquifer and D-C zone near Paulden (fig. E6) indicates similar or overlapping recharge source areas and a common outlet flowpath. Along the outlet flowpath, the carbonate aquifer functions primarily as a conduit, as opposed to a new source of ground water. That Na, Li, and B increase disproportionately along the flowpath, while Ca, $\delta^{18}\text{O}$, and δD values vary relatively little, points to water-rock interaction with rocks chemically similar to the Bright Angel Shale or Chino Valley Formation as opposed to mixing—although a small amount of mixing with the M-D sequence on the order of about 15 percent or less cannot be ruled out. Variations in the concentrations of elements are attributed to differences in ground-water residence time, or to slight differences in the length or direction of the flowpath, or to variations in the mineralogy of individual rock units. Geochemical trends presented here indicate preferential flow from the Big Chino aquifer near Paulden through fractures in basalt and karst in the D-C zone of the carbonate aquifer, to upper Verde River springs. In the following chapter, these geochemical trends will be further evaluated to calculate the relative contributions from each major aquifer to base flow in the upper Verde River.

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