

# GEOCHEMISTRY OF GROUND WATER IN ALLUVIAL BASINS OF ARIZONA AND ADJACENT PARTS OF NEVADA, NEW MEXICO, AND CALIFORNIA

## REGIONAL AQUIFER-SYSTEM ANALYSIS



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# Geochemistry of Ground Water in Alluvial Basins of Arizona and Adjacent Parts of Nevada, New Mexico, and California

*By* FREDERICK N. ROBERTSON

REGIONAL AQUIFER-SYSTEM ANALYSIS—  
SOUTHWEST ALLUVIAL BASINS, ARIZONA AND ADJACENT STATES

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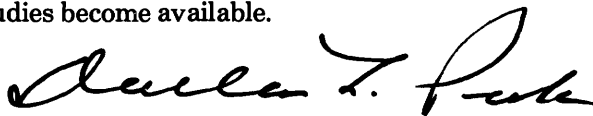


## FOREWORD

### THE REGIONAL AQUIFER-SYSTEM ANALYSIS PROGRAM

The Regional Aquifer-System Analysis (RASA) Program was started in 1978 following a congressional mandate to develop quantitative appraisals of the major ground-water systems of the United States. The RASA Program represents a systematic effort to study a number of the Nation's most important aquifer systems, which in aggregate underlie much of the country and which represent an important component of the Nation's total water supply. In general, the boundaries of these studies are identified by the hydrologic extent of each system and accordingly transcend the political subdivisions to which investigations have often arbitrarily been limited in the past. The broad objective for each study is to assemble geologic, hydrologic, and geochemical information, to analyze and develop an understanding of the system, and to develop predictive capabilities that will contribute to the effective management of the system. The use of computer simulation is an important element of the RASA studies, both to develop an understanding of the natural, undisturbed hydrologic system and the changes brought about in it by human activities, and to provide a means of predicting the regional effects of future pumping or other stresses.

The final interpretive results of the RASA Program are presented in a series of U.S. Geological Survey Professional Papers that describe the geology, hydrology, and geochemistry of each regional aquifer system. Each study within the RASA Program is assigned a single Professional Paper number, and where the volume of interpretive material warrants, separate topical chapters that consider the principal elements of the investigation may be published. The series of RASA interpretive reports begins with Professional Paper 1400 and thereafter will continue in numerical sequence as the interpretive products of subsequent studies become available.

A handwritten signature in black ink, appearing to read "Dallas L. Peck". The signature is fluid and cursive, with a large, stylized initial 'D'.

Dallas L. Peck  
Director



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## METRIC CONVERSION FACTORS

For readers who wish to convert measurements from the inch-pound system of units to the metric system of units, the conversion factors are listed below:

Multiply inch-pound units	By	To obtain metric units
inch (in)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )
acre-foot (acre-ft)	0.001233	cubic hectometer (hm <sup>3</sup> )
cubic foot per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second (m <sup>3</sup> /s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
degree Fahrenheit (°F)	°C=(temp °F-32)/1.8	degree Celsius (°C)

## ALTITUDE DATUM

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



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By FREDERICK N. ROBERTSON

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ABSTRACT

Chemical and isotope analyses of ground water from 28 basins in the Basin and Range physiographic province of Arizona and parts of adjacent States were used to evaluate ground-water quality, determine processes that control ground-water chemistry, provide independent insight into the hydrologic flow system, and develop information transfer. The area is characterized by north- to northwest-trending mountains separated by alluvial basins that form a regional topography of alternating mountains and valleys. On the basis of ground-water divides or zones of minimal basin interconnection, the area was divided into 72 basins, each representing an individual aquifer system. These systems are joined in a dendritic pattern and collectively constitute the major water resource in the region.

Geochemical models were developed to identify reactions and mass transfer responsible for the chemical evolution of the ground water. On the basis of mineralogy and chemistry of the two major rock associations of the area, a felsic model and a mafic model were developed to illustrate geologic, climatic, and physiographic effects on ground-water chemistry. Two distinct hydrochemical processes were identified: (1) reactions of meteoric water with minerals and gases in recharge areas and (2) reactions of ground water as it moves down the hydraulic gradient. Reactions occurring in recharge and downgradient areas can be described by a 13-component system. Major reactions are the dissolution and precipitation of calcite and dolomite, the weathering of feldspars and ferromagnesian minerals, the formation of montmorillonite, iron oxyhydroxides, and probably silica, and, in some basins, ion exchange.

The geochemical modeling demonstrated that relatively few phases are required to derive the ground-water chemistry; 14 phases—12 mineral and 2 gas—consistently account for the chemical evolution in each basin. The final phases were selected through analysis of X-ray diffraction and fluorescence data, aqueous speciation and saturation data, and mass-balance and isotopic constraints and through chemical models developed from mineral combinations among the 27 phases that were considered realistic in these geologically and mineralogically complex basins. X-ray diffraction of basin-fill sediments confirm the presence of the postulated minerals and their weathering sequences.

High partial pressures of soil CO<sub>2</sub> and large concentrations of dissolved CO<sub>2</sub> in recharge areas, and the rapid depletion of CO<sub>2</sub> downgradient, accompanied by high weathering rates of the silicates which also decrease downgradient, indicate that carbonic acid is the impetus in the weathering process. Reactions in the soil zone and the unsaturated zone are influential and, in some instances, are as important as the mineralogy of the source rock in determining ground-water compositions.

The basins can be divided geochemically into two general categories—closed systems, which evolve under closed hydrologic conditions, and open systems, which are open to CO<sub>2</sub> and other constituents along the flow path. The ground-water chemistry of the unconfined aquifers in the eastern part of the study area and of the aquifers underlying the flood plain along the Colorado River generally evolves under open conditions. The ground-water chemistry of most basins in the central and western parts and of the confined aquifers in the eastern part evolves under closed conditions. The factors that determine whether a basin is an open or closed system are the amount of and the spatial and seasonal distribution of annual precipitation and the presence or absence of fine-grained confining units.

The basins along the Colorado River are unique among basins in the region. Virtually all ground water underlying the flood plain originated as seepage or overbank flow from the Colorado River. Initial deuterium content of about -120 per mil is indicative of precipitation from the central part of Colorado. Using chemical models derived from other basins, weathering and dissolution reactions were defined but not with the same consistency, suggesting the presence of other mineral phases or reactions. The commonly observed increases in sulfate and chloride concentrations and the lower sulfate to chloride ratios of the ground water relative to the river water, however, probably are not a function of evapotranspiration and sulfate reduction, as is proposed in the literature. The chemical and isotope data indicate that dissolution of halite and gypsum is the major cause of changes in water chemistry in these basins along the river.

The oxidizing nature of the ground water greatly increases the solubility of several trace elements. Fluoride, hexavalent chromium, arsenic, boron, barium, selenium, lead, and nitrogen as nitrate may occur in concentrations that exceed State and Federal maximum contaminant levels. Fluoride, hexavalent chromium, arsenic, nitrate, and boron present environmental problems in several basins. Sources

and controls for these elements were determined or postulated through statistical and graphic techniques, geologic information, and equilibrium models.

Through the use of the geochemical models, climatic and geologic data, and analytical data of the basin-fill sediments, information transfer was developed for prediction of water quality and geochemistry throughout most of the area.

## INTRODUCTION

The U.S. Geological Survey, in response to a congressional decision to appraise the Nation's ground-water resources, began the Regional Aquifer-System Analysis (RASA) Program in 1978 to study and define the Nation's most important aquifer systems. The RASA program represents a systematic effort to evaluate the ground-water resources that underlie most of the Nation and are a major component of the Nation's total water supply. Previous hydrologic investigations of regional aquifers commonly have been limited in scope because of political subdivisions and the physical enormity of many hydrologic systems. The RASA program was designed to circumvent such difficulties by providing sufficient personnel and time for a comprehensive analysis of the respective hydrologic system.

The Southwest Alluvial Basins (Swab) RASA was implemented to evaluate the ground-water resources in the alluvial basins of Arizona and parts of those basins that extend into California, Nevada, and New Mexico. Objectives of the overall study were to define the extent of the ground-water system, the amount of water in storage, the amount of recharge to the ground water, the quality of the ground water, and the effects of ground-water development (Anderson, 1980). The regional aquifer of the Swab/RASA study area differs from most other regional aquifers in that the hydrologic system comprises 72 independent alluvial basin aquifers. These 72 separate aquifers do not form a single, areally extensive aquifer system; they nonetheless constitute the major regional water resource when considered collectively. Ground water, the most important source of water in this region, occurs mainly in these alluvial basins.

## PURPOSE AND SCOPE

The purposes of the geochemistry part of the Swab/RASA investigation were to (1) evaluate overall quality of the ground water, (2) determine probable sources of dissolved species, (3) determine spatial distribution of major solutes, (4) determine occurrences and solubility controls of trace and minor elements, (5) quantify geochemical processes that control ground-water chemistry, (6) examine a variety of chemical and isotope data to provide insight into the hydrologic systems, and

(7) provide information transfer from basins that have been more intensively studied to basins that are undeveloped or have complex geochemical histories.

This report summarizes onsite investigations and geochemical sampling programs that were conducted throughout the study area and describes the general geology and hydrology of the area, with emphasis on their impact on the regional geochemistry. The chemistry and mineralogy of the rocks that form the mountains, and of the basin fill in several basins, are described and related to the chemical evolution of the ground water. Geochemical models were developed to define the reactions responsible for evolution of the ground-water chemistry and were used to evaluate the geochemistry in basins of different hydrologic and physiographic settings. This report is directed primarily to geochemists but also is intended for hydrologists and other scientists and engineers concerned with water quality.

## APPROACH

The approach of the study was to collect pertinent geochemical and water-quality data in selected basins for interpretation of the geochemistry and definition of the water quality. A large part of the geochemical study was the acquisition of new data. Chemical and isotope data were collected in 28 basins from the Arizona-New Mexico border to the Colorado River. A comprehensive sampling program was initiated because of deficiencies in existing field measurements, trace-element data, and isotope data and because of diversity in physiography, geology, and water chemistry among basins. The basins selected were those having unique physiographic, geologic, hydrologic, or geochemical characteristics or those representative in these characteristics of numerous other basins. Geochemical and statistical computer codes were used for data interpretation. Through analysis of the newly acquired data, geochemical similarities and differences were defined. Definition of the geologic, hydrologic, and geochemical differences and similarities was essential for the development of information transfer because of the large number of basins within the study area. This transfer of information—the projection of geochemistry or of water quality—was subsequently used to define a larger number of basins.

## METHODS OF DATA COLLECTION AND ANALYSIS

Water samples were collected from more than 500 wells in 28 basins throughout the study area. All samples for major ion, trace-element, and isotope analysis were collected and preserved using procedures suggested by the U.S. Geological Survey Central Laboratory in



Denver, where the samples were subsequently analyzed. Temperature, pH, and alkalinity were determined in the field; fixed end-point titration was used for alkalinity determination. (See Barnes, 1964; Brown and others, 1970.)

The isotopic compositions presented in this paper are reported by  $\delta$  notation:

$$\delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 10^3, \quad (1)$$

where  $R$  is either the D/H,  $^{18}\text{O}/^{16}\text{O}$ , or  $^{13}\text{C}/^{12}\text{C}$  isotope ratio and all values are reported in per mil (‰). Positive values show the sample to be enriched in the heavy isotope species, and negative values show the sample to be depleted in the heavy isotope species relative to the standard. Deuterium ( $\delta\text{D}$ ) and oxygen ( $\delta^{18}\text{O}$ ) ratios are reported relative to Standard Mean Ocean Water (SMOW), and the carbon isotope ratios relative to Chicago Peedee Belemnite (PDB). The  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ , and tritium (reported in tritium units, TU) were analyzed by the U.S. Geological Survey Research Group in the northeastern region, Reston, Va. Precision of the  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{13}\text{C}$  analyses was  $\pm 1.0\text{‰}$ ,  $\pm 0.1\text{‰}$ , and  $\pm 0.1\text{‰}$ , respectively. Carbon-14 ( $^{14}\text{C}$ ) isotope samples were analyzed by the Radiocarbon Dating Laboratory, Laboratory of Isotope Geochemistry, University of Arizona, and reported in percent modern carbon. Samples for the  $^{14}\text{C}$  analysis were precipitated in the field or delivered to the laboratory within 24 hours for precipitation.

The Center for Meteorite Studies, Arizona State University, analyzed selected well cuttings and well cores for bulk mineralogy and chemistry. The Soils, Water, and Engineering Department, University of Arizona, analyzed the clay fraction of the cuttings and cores for clay minerals. The computer program WATEQ2 (Ball and others, 1980) was used to calculate equilibrium relations of the aqueous and mineral phases. Major ion and trace-element data were analyzed by linear-regression analysis to determine statistical significance between variables (Nie and others, 1975).

#### PREVIOUS WATER-QUALITY AND GEOCHEMICAL INVESTIGATIONS

Water-quality studies dealing primarily with dissolved-solids distributions or single constituents have been done in several basins in Arizona. Kister and Hardt (1966) investigated the salinity of ground water in western Pinal County. Kister prepared dissolved-solids maps for the Tucson area (1974b) and the Phoenix area (1974a). Kister and others (1966) prepared maps showing the fluoride content and salinity of ground water in the

Willcox basin, and Kister (1973) showed the dissolved-solids content of ground water and selected fluoride concentrations for the lower Colorado River region, Arizona, Nevada, New Mexico, and Utah. Smoor (1967) determined the hydrochemical facies of ground water in the Tucson basin. Osterkamp (1974) mapped the chemical quality of ground water for public supply in the Phoenix area, and Osterkamp and Laney (1974) mapped the chemical quality of water for public supply in the Tucson area. Laney evaluated the quality of water along the Gila River in Graham County (1970) and the chemical quality of water in the Tucson basin (1972). Laney (1977) studied the effects of phreatophyte removal on water quality in the Gila River area, Graham County. Simpson and others (1970) determined the seasonal recharge to ground water in the Tucson basin area by deuterium analysis. Winograd and Robertson (1982) investigated deep oxygenated ground water in the Basin and Range province of Nevada and Arizona, and Robertson (1975) evaluated the occurrences of hexavalent chromium in Paradise Valley. Olmsted and others (1973), Metzger and Loeltz (1973), and Metzger and others (1973) investigated the water resources and water quality in a comprehensive study along the Colorado River between Hoover Dam and the international boundary. Wallick (1973) used radiocarbon to date the ground water in the Tucson basin, and Parada (1981) determined the isotopic content of soil carbon dioxide in the Tucson basin. Schmidt (1979) evaluated ground-water quality in the major basins of Maricopa County, and Robertson (1984, 1986) determined the solubility controls of trace elements in alluvial basins of Arizona. Robertson and Garrett (1988) mapped the distribution of fluoride in ground water in alluvial basins of Arizona and parts of adjacent States.

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thanks the hundreds of farmers, ranchers, and other well owners, whose cooperation and assistance made possible the field investigations and collection of data.

#### PHYSIOGRAPHY AND DRAINAGE

The study area encompasses about 82,000 mi<sup>2</sup> (square miles) of the Basin and Range physiographic province (Fenneman, 1931) in Arizona and small parts of the adjacent States of California, Nevada, and New Mexico. The area was subdivided on the basis of hydrologic characteristics into the Central highlands water province and the Basin and Range lowlands water province (U.S. Geological Survey, 1969) (fig. 1).

The study area is characterized by generally north- to northwest-trending mountains separated by wide alluvial basins that form a regional topography of alternating mountains and valleys. Altitudes range from 150 ft (feet) above sea level near Yuma to more than 11,000 ft above sea level in the Central highlands. Although a common geologic structure prevails throughout the Basin and Range province, physical differences exist between the Central highlands and the Basin and Range lowlands.

The valleys in the central and southwestern parts of the Basin and Range lowlands between Phoenix and Yuma are more extensive than in other parts of the study area, encompassing about 80 percent of the local terrain. The mountain ranges are small, deeply dissected, and rimmed by large pediments that form typically large oval basins. The valley floors range in altitude from less than 200 to about 2,000 ft above sea level, and the mountains bounding the valleys rise an additional 1,000 to 2,000 ft above the valley floor. The valleys in the northwestern and southeastern parts of the Basin and Range lowlands are characterized by long north-trending valleys and mountains that are approximately equal in areal extent. The mountain ranges are moderately dissected, and the valleys have pronounced slopes that extend from the mountains to the basin axis. The altitude of the valley floors ranges from about 2,500 ft in Detrital Valley in the northwest (location of valleys and other geographic areas shown in fig. 5) to about 4,000 ft in the Willcox basin in the southeast, with adjacent mountains rising as much as 6,000 ft above the valley floors.

In contrast to the Basin and Range lowlands, the Central highlands are mountainous and contain shallow intermontane basins that occupy only a small part of the total area. With the exception of Verde and Big Chino Valleys, the basins commonly contain little more than a thin veneer of alluvium along a stream channel.

Six major river systems—the Colorado, Salt, Gila, Santa Cruz, San Pedro, and Verde Rivers—drain the area from east to west (fig. 1). The Colorado River originates in Colorado and flows southwestward across

Utah and Arizona and southward along the Arizona border to the Gulf of California. The Gila River and its tributary the Salt River originate in the highlands near the New Mexico-Arizona border and flow westward to join near Phoenix. The Gila River is tributary to the Colorado River near Yuma. The Verde River originates in the highlands and joins the Salt River near Phoenix. The San Pedro River originates in Mexico and flows northward to join the Gila River. The Santa Cruz River originates near the international boundary and flows northward to join the Gila River west of Phoenix.

#### CLIMATE

The climate of the area is arid to semiarid, and precipitation generally is dependent on altitude, which increases in a northeasterly direction. Mean annual precipitation ranges from less than 3 in (inches) near Yuma to more than 30 inches in the higher altitudes of the Central highlands and of the eastern part of the area. Precipitation is highly variable and in any given year may depart greatly from the mean. Mean annual lake evaporation ranges from less than 60 inches in the higher altitudes of the Salt, Verde, and Gila Rivers to about 86 in along the Colorado River near Yuma (Anderson and others, written commun., 1986).

Two periods of precipitation are related to atmospheric flow patterns and pressure systems that draw quantities of moisture over the area. One system originates to the northwest over the Pacific Ocean providing winter precipitation, and the other originates to the south over the Gulf of Mexico and the Gulf of California providing summer precipitation. Winter precipitation generally is the result of regional storms of low intensity and long duration. Summer precipitation occurs as high-intensity short-duration thunderstorms that are localized and frequent. The amounts of precipitation for each period differ depending on location. Summer precipitation supplies about two-thirds of the total precipitation in the eastern part of Arizona but decreases to less than one-third in the western part (University of Arizona, undated). The amount of precipitation is highly variable within a basin; areas near mountains receive precipitation more frequently and in larger amounts than the central parts of the basin.

In contrast to rainfall, mean temperatures in the study area are consistent and vary little from year to year. Mean temperatures in July range between 80 and 90 °F in the northwestern and southeastern parts of the Basin and Range lowlands and between 90 and 95 °F in the southwestern part. Mean temperatures in January range between 40 and 50 °F in the northwestern and southeastern parts and between 50 and 60 °F in the southwestern part. Mean temperatures in July range between 70 and

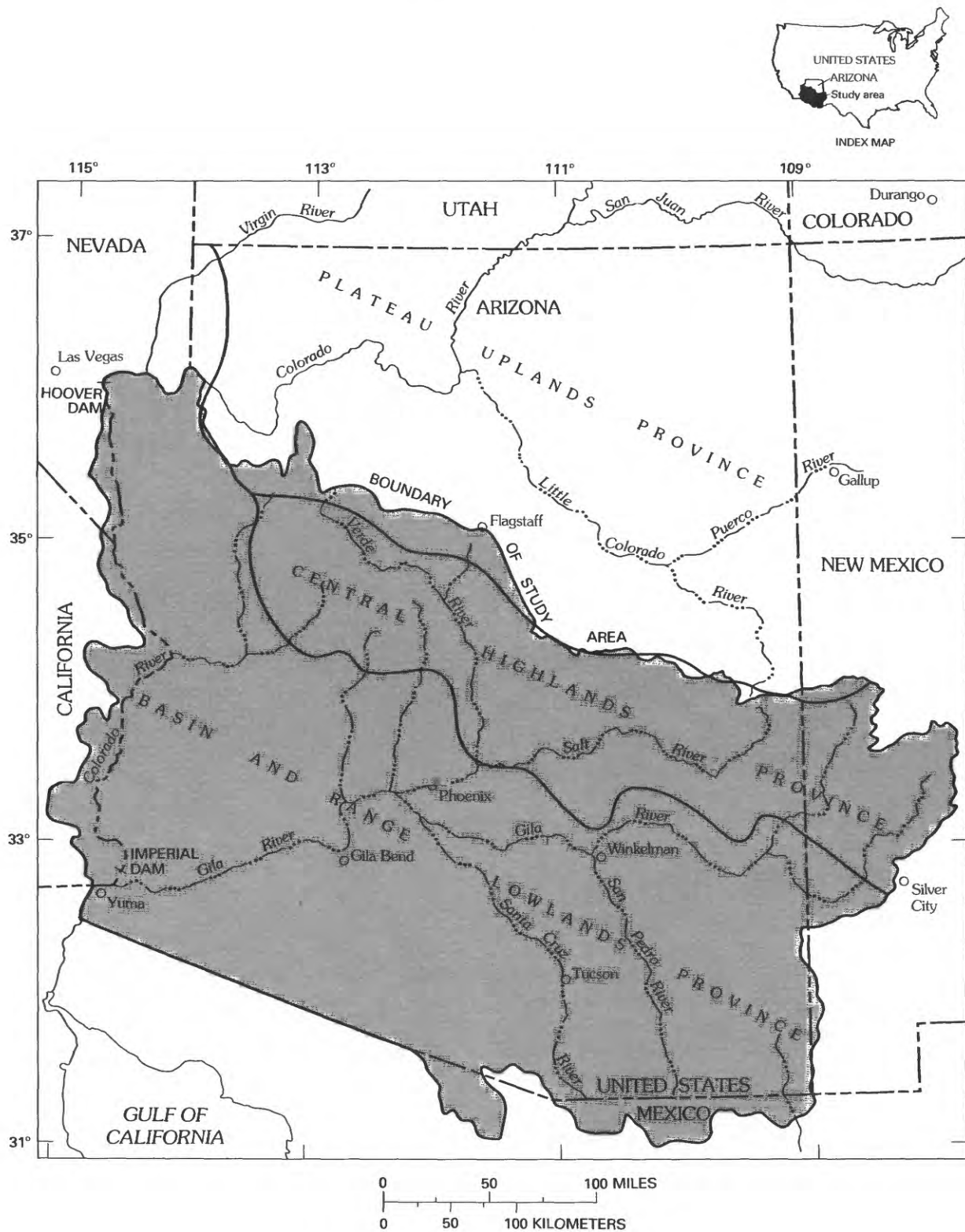


FIGURE 1.—Area of study and water provinces.

80 °F in the Central highlands and in January are generally below 40 °F (Dunbier, 1970).

### WELL-NUMBERING SYSTEM

Well identification and location are indicated by the well-numbering system used by the U.S. Geological Survey and the U.S. Bureau of Land Management in Arizona (fig. 2).

### GEOLOGIC SETTING

The present-day physiography characterized by mountains and basins was formed primarily by large-scale normal faulting during the Basin and Range disturbance 14 to 6 million years ago (Scarborough and Peirce, 1978). Structural movement resulted in a series of upthrown and downthrown blocks throughout a large region in Arizona and nearby States. Block faulting altered previous drainage patterns, and the subsiding areas became depositional sites for locally derived sediments. Concurrent with this faulting, erosion and subsequent deposition of basin fill sculptured the mountains and formed the basins and valleys that now exist. The mountains consist mainly of consolidated intrusive and metamorphic rocks of Precambrian, Mesozoic, and Tertiary age. Volcanic and sedimentary rocks of Tertiary age also are common in many ranges. Volcanic and sedimentary rocks of Paleozoic and Mesozoic age occur in parts of a few ranges but are less abundant. The basins in the study area contain alluvial deposits and volcanic rocks of late Cenozoic age (Wilson and others, 1969).

### PRE-CENOZOIC ROCKS

The pre-Cenozoic rocks that form the major mountain ranges are divided broadly into intrusive, metamorphic, and volcanic rocks. Intrusive rocks of Precambrian age include granite, quartz monzonite, granodiorite, quartz diorite, and, locally, gabbro. Metamorphic rocks of Precambrian age include phyllite, mica schist, chlorite schist, amphibolite, and gneiss. These rocks are most abundant in the Central highlands and adjacent areas where they partially bound several major basins and form the largest ranges having the highest altitudes (Wilson and others, 1969). Intrusive and volcanic rocks of Mesozoic age are scattered throughout the central, western, and southwestern parts of the study area. Paleozoic rocks of predominantly marine limestone and mudstone crop out along the Colorado Plateau in the Central highlands and locally in the southeastern part of the study area. Isolated outcrops of Paleozoic rocks occur in west-central Arizona (Shafiqullah and others, 1980). Sed-

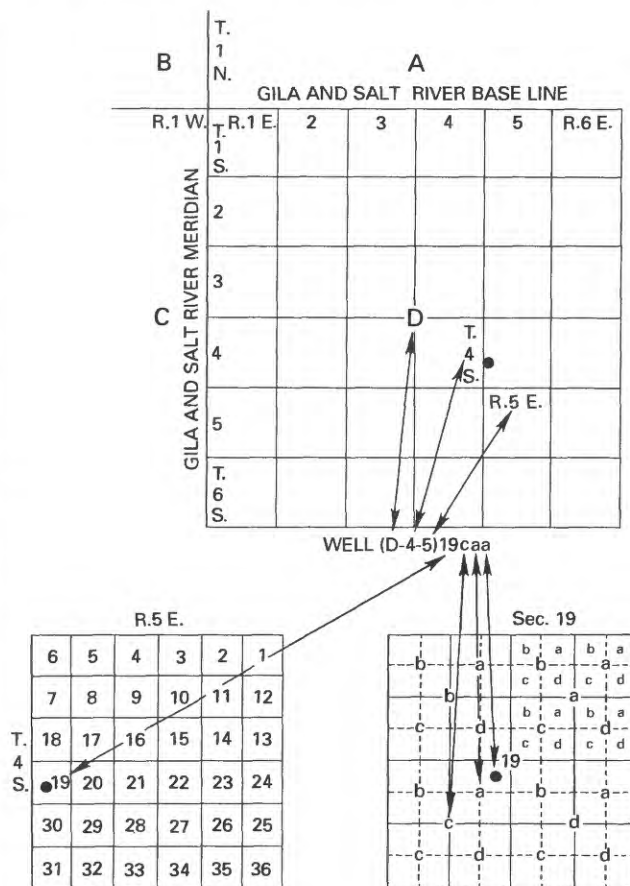


FIGURE 2.—Well-numbering system in Arizona. The well numbers used by the U.S. Geological Survey in Arizona are in accordance with the Bureau of Land Management's system of land subdivision. The land survey in Arizona is based on the Gila and Salt River meridian and base line, which divide the State into four quadrants. These quadrants are designated counterclockwise by the capital letters A, B, C, and D. All land north and east of the point of origin is in A quadrant, that north and west in B quadrant, that south and west in C quadrant, and that south and east in D quadrant. The first digit of a well number indicates the township, the second the range, and the third the section in which the well is situated. The lower case letters a, b, c, and d after the section number indicate the well location within the section. The first letter denotes a particular 160-acre tract, the second the 40-acre tract, and the third the 10-acre tract. These letters also are assigned in a counterclockwise direction, beginning in the northeast quarter. If the location is known within the 10-acre tract, three lowercase letters are shown in the well number. In the example shown, well (D-4-5)19caa designates the well as being in the NE $\frac{1}{4}$ NE $\frac{1}{4}$ SW $\frac{1}{4}$  sec. 19, T. 4 S., R. 5 E. Where more than one well is within a 10-acre tract, consecutive numbers beginning with 1 are added as suffixes.

imentary rocks of Mesozoic age of continental origin are found in places in southeastern Arizona. The rocks were structurally deformed, intruded by magmas, and overlain by younger sedimentary rocks during the late Mesozoic and early Cenozoic (Paleocene) as a result of the



Sevier and Laramide orogenies. Rocks formed during the Laramide orogeny are areally extensive and include rich porphyry copper deposits in parts of south-central Arizona (Wilson and others, 1969; Shafiqullah and others, 1980).

#### CENOZOIC ROCKS

Three major geologic events followed the Laramide orogeny during the Cenozoic Era: (1) the Mid-Tertiary orogeny, which was accompanied by calc-alkaline volcanism and plutonism and the accumulation of sediments; (2) the Basin and Range disturbance, which was accompanied by andesitic-basaltic volcanism, block faulting, basin formation, and sedimentation; and (3) maximum basin filling, which was followed by uplift, valley erosion, and development of terraces along major rivers (Scarborough and Peirce, 1978).

The Mid-Tertiary orogeny was characterized by crustal melting, plutonism, and extrusion of intermediate to silicic lavas. The volcanic rocks formed during the orogeny are areally extensive and are predominantly andesitic, rhyolitic, and dacitic in composition. Rhyolitic volcanic rocks form most of the Chiricahua Mountains and parts of the Galiuro and Winchester Mountains in the southeast, the Superstition Mountains near Phoenix, and the Tucson and Roskrige Mountains near Tucson. Intermediate volcanic rocks, transitional in chemical composition between mafic and felsic rocks, form large parts of the Galiuro and Winchester Mountains and are predominant in the Sand Tank Mountains near Vekol Valley and adjacent areas of the Papago Indian Reservation in south-central Arizona. (See Scarborough and Peirce, 1978.)

Following the Mid-Tertiary orogeny, thick sequences of pre-Basin and Range sedimentary rocks of Tertiary age were deposited in places. These rocks of continental origin range from boulder conglomerate to mudstone and generally are well indurated. Their areal distribution and clast type indicate depositional environments unrelated to the present-day geology of the surrounding mountains. The rocks are highly deformed, faulted, and tilted and generally are found at the basin margins in fault contact with older and younger rocks. These pre-Basin and Range sedimentary rocks are present in many basins beneath the basin fill (Laney and Hahn, 1987).

Most of the rocks in the alluvial basins in the study area were deposited after the Basin and Range disturbance and are Quaternary to late Tertiary in age. The basins were created in response to an east-northeast to west-southwest regional extension field that resulted in a network of north- to northwest-trending horsts and grabens bounded by high-angle normal faults. The subsidence of these grabens and subsequent erosion resulted

in late Cenozoic basin-fill deposits that exceed thicknesses of 8,300 ft (Scarborough and Peirce, 1978).

#### BASIN-FILL DEPOSITS

Basin-fill deposits include clastic sediments, evaporites, interbedded volcanic rocks, stream alluvium, and flood-plain deposits. The deposits occur as distinct beds of sand and gravel and as poorly sorted interbedded clayey silt, sand, and gravel locally interbedded with volcanic rocks. Deposits near the basin margins commonly are fanglomerate or fluvial sand and gravel that grade laterally into silt, clay, and evaporites near the center of the basin. The amount of fine-grained silt and clay material (less than 0.0625 mm (millimeter) in diameter) in the deposits near the basin margins ranges from about 10 to 50 percent but may increase toward the center of the basin to more than 90 percent. Fine-grained deposits and evaporites that lie in basin centers accumulated in internal or restricted drainage environments.

Deposition of the basin fill was controlled primarily by tectonic processes. Erosion of upthrown areas and concurrent deposition of sediments resulted in the basinward increase in fine-grained sediments and occurrences of the thick, fine-grained deposits in the deepest structural parts of the basins. The transition from coarse-grained to fine-grained deposits generally occurred near fault boundaries but varied from place to place because of such factors as size of the drainage area, amount of precipitation on the drainage area, relief of the depositional area, structural movement, and shifting of the stream channels during deposition. Gradual development of integrated or through-flowing drainage also influenced grain-size distribution. The generalized structure and stratigraphy of a typical alluvial basin in the study area are shown in figure 3.

On the basis of source area, particle size, age, composition, and degree of cementation, the basin-fill deposits are informally divided into three general units: (1) lower basin fill, (2) upper basin fill, and (3) stream alluvium (Pool, 1986). These general units represent a depositional sequence that has been observed in many basins.

#### LOWER BASIN FILL

The lower basin fill was deposited under internal drainage conditions and consists of the finest grained and most indurated basin-fill sediments. The unit was deposited during active tectonism of the Basin and Range disturbance and consequently is the most highly faulted and deformed. The lower basin fill is subdivided into older and younger parts on the basis of content and texture.

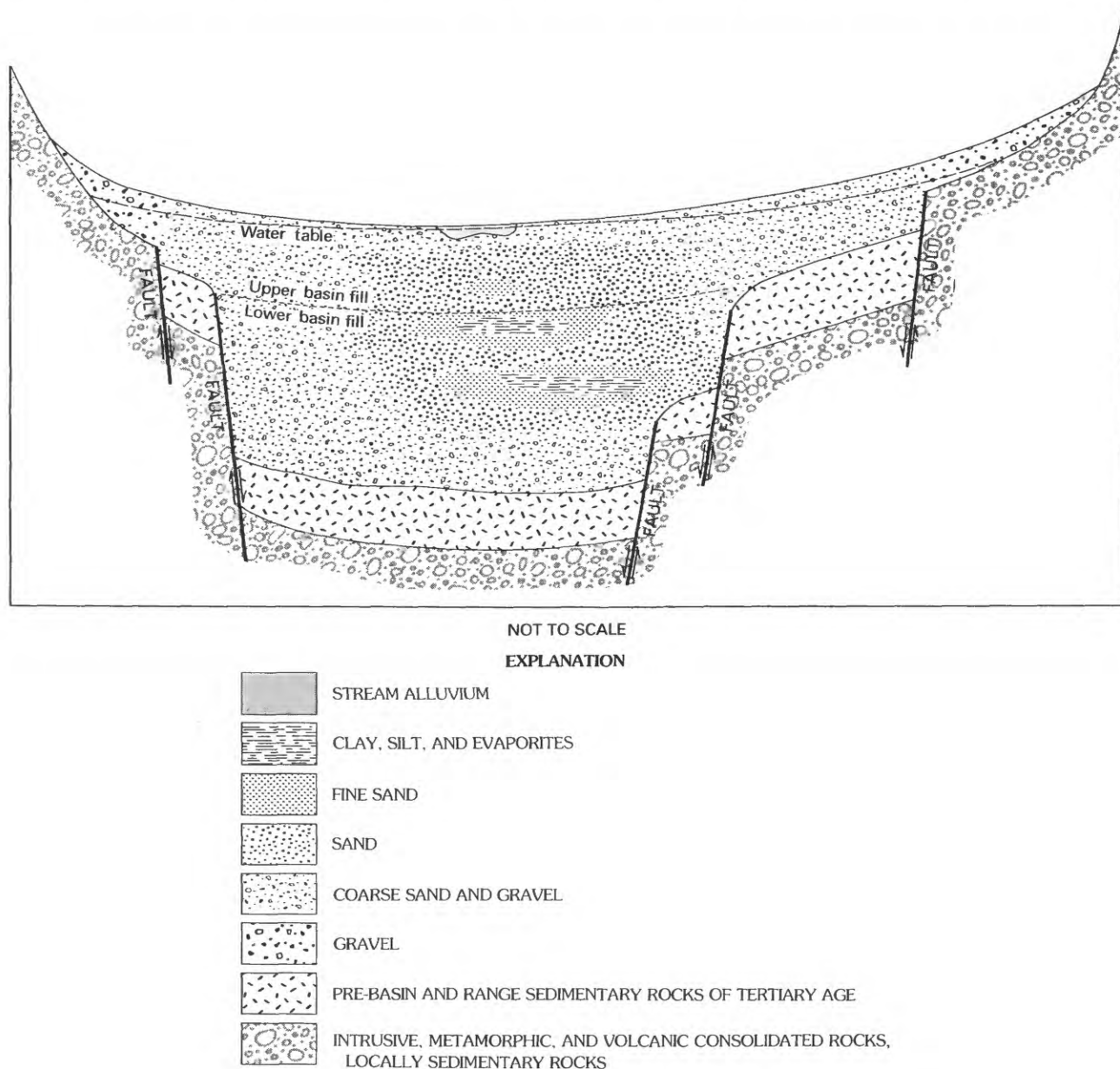


FIGURE 3.—Generalized structure and stratigraphy of a typical alluvial basin in the study area.

The older part of the lower basin fill consists of siltstone, evaporites, and intercalated basalt sequences and is moderately to well cemented with calcium carbonate. Massive evaporite sequences that are thousands of feet thick occur in places in the older unit. Thick evaporites in the older part have been penetrated by drilling in several deep basins adjacent to the Central highlands—4,000 ft of halite near Red Lake in Hualapai Valley, 3,600 ft of halite in West Salt River Valley, 5,985 ft of anhydrite in the Eloy area, and 600 ft of gypsum in the Safford basin. In addition to these massive deposits, 1,500 ft of interbedded gypsum and mudstone is present in the Douglas basin, 1,300 ft of interbedded gypsum,

silt, and clay in lower San Pedro Valley, and several hundred feet of interbedded silt, clay, and gypsum in Paradise Valley (Eberly and Stanley, 1978; Scarborough and Peirce, 1978). Fine-grained gypsiferous deposits of the lower basin fill also occur at depths of less than 1,000 ft in Ranegras Plain and McMullen Valley.

The younger part of the lower basin fill consists of clay and silt with lenses of sand and gravel; it is less consolidated and contains fewer volcanic rocks than the older part. The coarse sand and gravel facies are found in several basins at depths as shallow as 500 to 700 ft below land surface. Coarse-grained facies underlie Vekol Valley, Ranegras Plain, Harquahala Plain, McMullen Val-

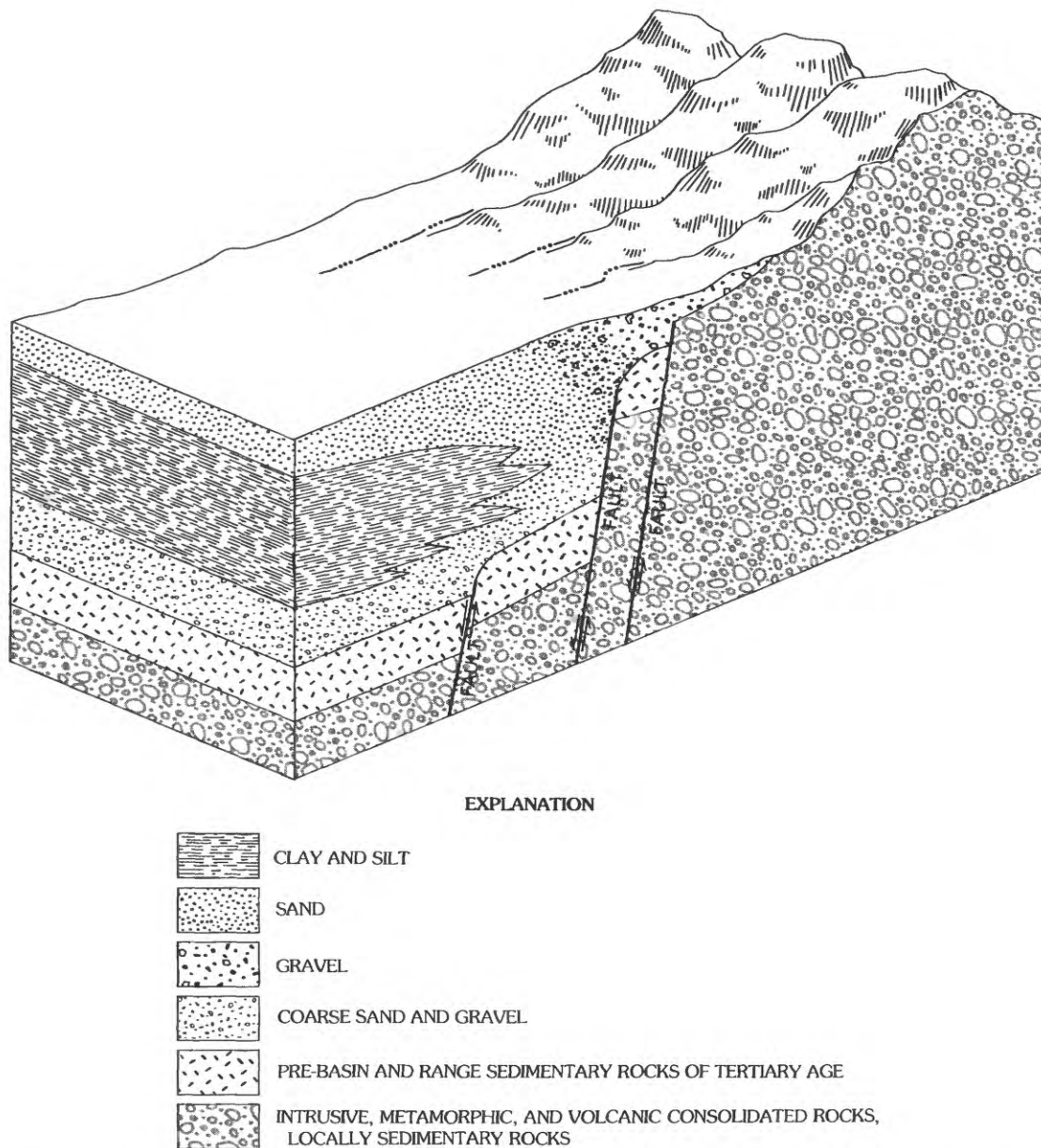


FIGURE 4.—Generalized position and extent of the coarse-grained and fine-grained facies in the lower basin fill.

ley, Butler Valley, and Bullard Wash and commonly are overlain by fine-grained sediments of the lower basin fill. Coarse-grained facies of the lower basin fill also are found in the eastern part of the study area in the lower San Pedro and San Simon Valleys and Safford basin (Pool, 1986). The position and extent of these facies in the lower basin fill are generalized in figure 4.

#### UPPER BASIN FILL

The upper basin fill was deposited near the end of the Basin and Range disturbance and thus is considerably less deformed, tilted, and faulted than the lower basin

fill. The unit generally is coarser grained and less cemented than the lower basin fill and is characterized by grain-size distributions that are less coincident with fault boundaries. Fine-grained facies where they occur are less areally extensive than those in the lower basin fill. Moderately coarse grained facies of the upper basin fill are as much as 1,000 ft thick in several basins in the central and eastern parts of the area (Brown and Schumann, 1969; Davidson, 1973a; Laney and Hahn, 1987). The upper basin fill also occurs in the western part of the study area but generally is less than 100 ft thick. Fine-grained facies of the upper basin fill also occur in



southeastern basins as lacustrine deposits of clay, silt, sand, and some limestone (Pool, 1986).

The sediments of the upper basin fill were laid down, for the most part, in closed-basin depositional environments, as were those of the lower basin fill. In some basins, however, grain-size distributions represent complex depositional environments that may include through-flowing drainage from one basin to another. Depositional features less coincident with the basin configuration and fault boundaries, the absence of evaporites, and the abundance of rounded clasts unrelated to adjacent mountains indicate that sediments of the upper part of the upper basin fill may have accumulated at a time when through-flowing drainage conditions were prevalent (Laney and Hahn, 1987).

#### STREAM ALLUVIUM

Stream alluvium occurs as narrow bands of alluvial deposits generally less than 100 ft thick along most streams that drain the study area. Thick sections of stream alluvium occur only along the Salt, Gila, Santa Cruz, Verde, San Pedro, and Colorado Rivers. The deposits are as much as 300 ft thick along the Salt and Gila Rivers in the Phoenix area (Laney and others, 1978; Laney and Hahn, 1987) and as much as 700 ft thick along the Colorado River. They range in width from several hundred feet to a maximum of about 10 mi (miles) along the Colorado River. The thick and areally extensive flood-plain deposits along the Colorado River have been divided into older and younger alluviums (Metzger and Loeltz, 1973; Metzger and others, 1973; Olmsted and others, 1973). These units overlie the Bouse Formation, which is a marine deposit of Miocene and Pliocene age formed in an embayment of the Gulf of California. The Bouse Formation was incised and overlain by stream alluvium when the Colorado River established its present configuration during the Pliocene (Shafiqullah and others, 1980).

#### REGIONAL HYDROLOGY

The regional ground-water flow system closely parallels the direction of the surface-water drainage. Ground water in areas north and south of the Gila River generally flows toward the Gila and along the Gila River drainage. Ground water in basins that adjoin the Colorado River flows toward the river, and ground water in a few individual basins along the international boundary flows southward into Mexico. The intrusive and metamorphic rocks and most of the volcanic rocks that separate the basins generally are impermeable and transmit little, if any, water. Where basins are hydraulically interconnected, ground water moves from the basin of

higher altitude to the basin of lower altitude. Basins are hydrologically interconnected where the alluvium overlying the consolidated or other impermeable rocks along ground-water divides is saturated. Most of the basins in the study area are connected hydraulically; only the Willcox basin is internally drained. On the basis of ground-water divides or zones of minimal hydrologic basin interconnection, the study area was divided into 72 basins or individual alluvial aquifers that are joined in a dendritic pattern and constitute the regional aquifer system (fig. 5).

#### OCCURRENCE OF GROUND WATER

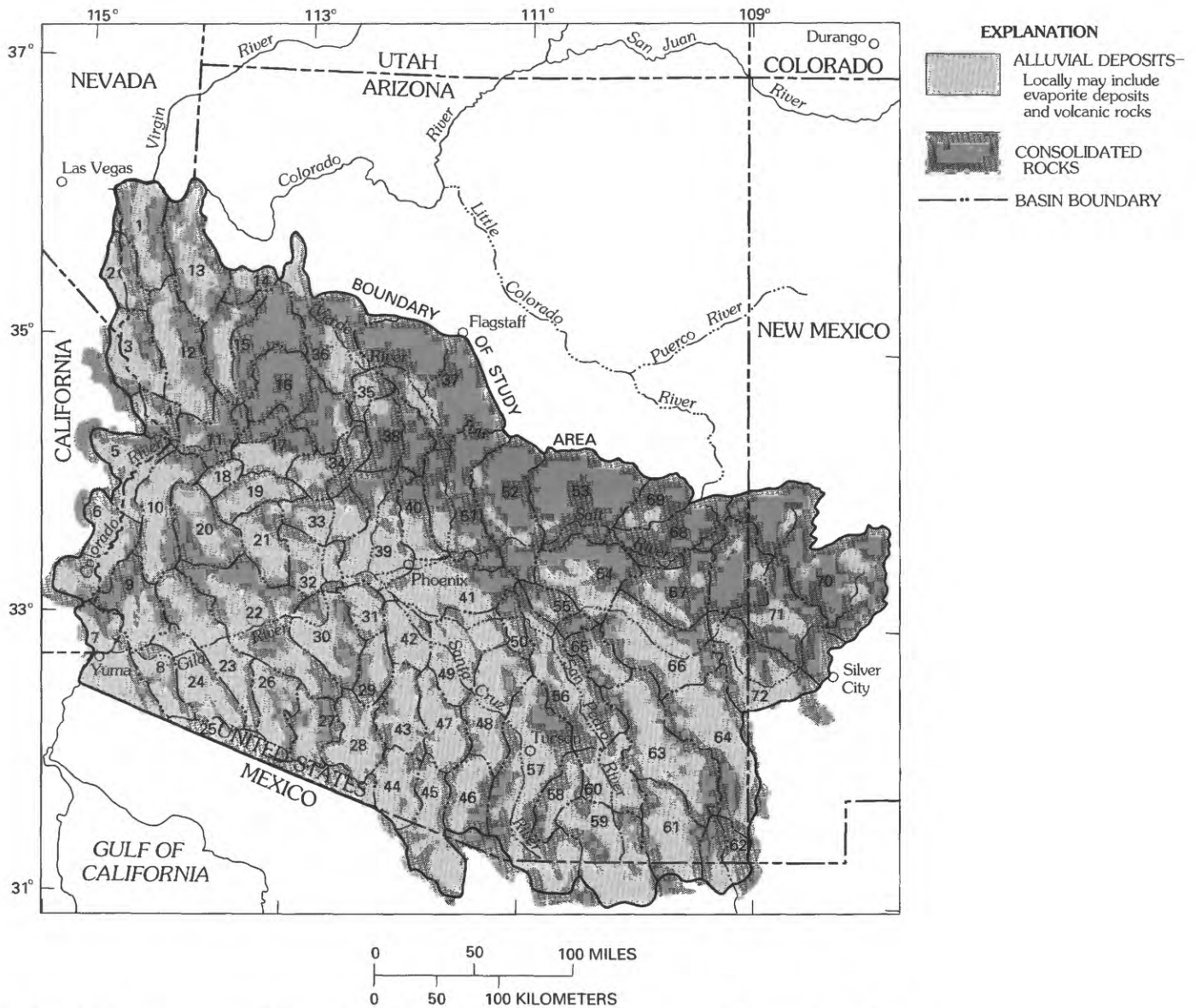
Ground water occurs in the study area in rocks of all principal types: intrusive, metamorphic, and volcanic rocks; pre-Basin and Range sedimentary rocks of Tertiary age; and basin-fill sediments. The water-bearing properties of these rocks, however, vary widely. Well yields range from a few gallons per minute (gal/min) to more than 6,000 gal/min.

The water-bearing characteristics of the intrusive, metamorphic, and volcanic rocks are dependent on localized joint fractures and weathering characteristics. In general, well yields of intrusive and metamorphic rocks are limited to a few gallons per minute. Volcanic rocks, which can be more porous and fractured, may yield more water and serve as local sources, but, like intrusive rocks, their water-yielding properties generally are limited. Volcanic rocks are the source for the municipal water supply for the city of Kingman, Ariz. (Gillespie and Bentley, 1971), and ground-water flow through fractured volcanic rocks has been reported on the Papago Indian Reservation (Heindl, 1967). Although the intrusive, metamorphic, and volcanic rocks generally contain little water, they may indirectly influence the hydraulic conductivity or recharge of the alluvial aquifers. Intrusive granitic rocks are more likely to weather to permeable quartz-rich sandy soils, whereas volcanic rocks are more likely to weather to tight clayey deposits. The weathering process therefore may form deposits of differing hydraulic conductivity or deposits that may enhance or preclude infiltration.

The pre-Basin and Range sedimentary rocks of Tertiary age that underlie some of the basins locally may yield copious water to wells. Because the rocks often lie at great depth and are well indurated, structurally deformed, and discontinuous throughout the area, however, they generally are not an important water-bearing unit.

The permeable, coarse-grained basin-fill deposits contain vast amounts of recoverable ground water and are the main water-bearing units. The high porosity and permeability of sand and gravel allow water to move





- |                                 |   |                            |                              |
|---------------------------------|---|----------------------------|------------------------------|
| 1 Detrital Valley               | 20 Ranegas Plain  | 37 Verde Valley            | 55 Dripping Springs basin    |
| 2 Lake Mohave area              | 21 Harquahala Plain                                       | 38 Agua Fria River area    | 56 Lower San Pedro Valley    |
| 3 Mohave Valley                 | 22 Palomas and Sentinel Plains                            | 39 West Salt River Valley  | 57 Upper Santa Cruz area     |
| 4 Chemehuevi Valley             | 23 King Valley and<br>San Cristobal Wash area             | 40 Paradise Valley         | 58 Sonoita basin             |
| 5 Parker Valley                 | 24 Mohawk Valley  | 41 East Salt River Valley  | 59 Upper San Pedro Valley    |
| 6 Palo Verde and Cibola Valleys | 25 Tule Desert, La Abra Plain, and<br>Sonoyta Valley area | 42 Maricopa-Stanfield area | 60 Benson area               |
| 7 Yuma area                     | 26 Growler Wash area                                      | 43 Santa Rosa Valley       | 61 Douglas basin             |
| 8 Lechuguilla Desert            | 27 Cuerda de Lena Wash area                               | 44 Tecolote Valley         | 62 San Bernardino Valley     |
| 9 Castle Dome Plain             | 28 San Simon Wash area                                    | 45 Baboquivari Wash area   | 63 Willcox basin             |
| 10 La Posa Plain                | 29 Vekol Valley   | 46 Altar Valley            | 64 San Simon Valley          |
| 11 Bill Williams River area     | 30 Gila Bend Plain  | 47 Viopuli Wash area       | 65 Aravaipa Valley           |
| 12 Sacramento Valley            | 31 Rainbow Valley   | 48 Avra Valley             | 66 Safford basin             |
| 13 Hualapai Valley              | 32 Lower Hassayampa basin                                 | 49 Eloy area               | 67 Bonita basin              |
| 14 Truxton basin                | 33 Upper Hassayampa basin                                 | 50 Donnelly Wash area      | 68 Black River basin         |
| 15 Big Sandy basin              | 34 Skull Valley   | 51 Lower Verde River area  | 69 White River basin         |
| 16 Santa Maria River area       | 35 Little Chino Valley                                    | 52 Tonto Creek area        | 70 Upper Gila River basin    |
| 17 Bullard Wash area            | 36 Big Chino Valley                                       | 53 Upper Salt River area   | 71 San Francisco River basin |
| 18 Butler Valley                |   | 54 San Carlos basin        | 72 Duncan basin              |
| 19 McMullen Valley              |   |                            |                              |

FIGURE 5.—Area of study divided into 72 basins.

freely from areas of higher to areas of lower hydraulic head. In contrast, the fine-grained sediments contain water, but the small grain size and consequently the molecular attraction restrict the flow of water. Water stored in fine-grained units of low permeability may be recovered if the units lie adjacent to permeable sand and gravel deposits.

#### GROUND-WATER FLOW SYSTEM

Depth to the water table varies widely throughout the study area but in all basins is greater near the mountain fronts. Depth to water near the mountains is typically 300 to 800 ft or more and decreases basinward to about 5 to 400 ft. The hydraulic gradient of the water table resembles that of the land surface but is somewhat gentler. Ground water moves perpendicular to the mountain fronts toward the basin axis, where it either discharges or blends with existing underflow. Ground-water velocities are on the order of a few feet to a few tens of feet per year. Velocities generally are greater near the mountain fronts, where gradients are steeper and permeabilities are higher than those in the interior of the basins.

Ground water generally occurs under unconfined conditions, but confined conditions may exist where extensive fine-grained facies of the basin-fill deposits are present and sufficient recharge occurs. Confined conditions and flowing wells, some of which discharge more than 600 gal/min, are found extensively in the eastern part of the study area in the Safford basin, the Benson area, lower San Pedro Valley, San Bernardino Valley, and San Simon Valley. Confined conditions also exist in Verde Valley (Owen-Joyce and Bell, 1983).

#### RECHARGE TO THE ALLUVIAL AQUIFERS

Ground water is recharged to the alluvial aquifers as (1) infiltration of precipitation and runoff along mountain fronts (mountain-front recharge), (2) infiltration along streams that generally traverse the central axis of basins (basin-center recharge), and (3) underflow from adjacent basins of higher altitude. The source of most of the ground water is precipitation that falls in the study area. Only basins along the Colorado River are recharged by water that does not originate within the study area.

Of the three modes of recharge, mountain-front recharge accounts for most of the ground water in storage. Mountain-front recharge occurs within an indeterminate zone that begins at the hardrock-alluvium contact and extends into the basin. A large part of the recharge probably occurs near the contacts in the numerous arroyos and coarse-grained alluvial fans that drain the mountains.

Infiltration along streams recharges the aquifers in several basins. The basins along the Colorado River receive virtually all their water from infiltration of river water directly into the alluvium. Along the Salt and Gila Rivers near Phoenix, surface water infiltrates the coarse-grained stream alluvium adjoining the rivers. Basin-center recharge probably occurs to some extent in other basins that contain major streams. The recharge provided by the smaller streams and washes probably is insignificant.

Underflow of ground water from adjacent basins of higher altitude contributes to the recharge of several basins in the south-central part of the study area. Underflow from Avra Valley (Moosburner, 1972) and the upper Santa Cruz area (Anderson, 1972) contributes to the recharge of the Eloy and Maricopa-Stanfield areas, and underflow from the southern part of the Willcox basin contributes to the recharge of the adjoining Douglas basin (Brown and Schumann, 1969). Ground-water underflow may be a small recharge component in some basins in the west-central part.

#### DISCHARGE FROM THE ALLUVIAL AQUIFERS

Ground-water discharge from basins occurs through (1) discharge to streams, (2) evapotranspiration from areas where the water table is shallow, (3) ground-water underflow out of the basin, and (4) ground-water pumping. Discharge to streams and discharge by evapotranspiration occur in basins that have gaining streams or shallow depths to water. Ground water that discharges by underflow moves downvalley and exits through a narrow alluvium-filled gap between the mountains. Because the shallowest water levels within a basin are found downvalley near this gap, evapotranspiration as well as underflow may occur in these areas. These natural processes of discharge have been altered in many basins by ground-water pumping, which in some basins is the dominant discharge mechanism. Pumping has lowered water levels as much as several hundred feet in some basins near Phoenix (Laney and others, 1978). The ground-water hydrology of a basin aquifer characterized by mountain-front recharge, ground-water movement, and natural ground-water discharge is illustrated in figure 6.

#### CHEMICAL CHARACTER OF THE GROUND WATER

The ground water in the study area, as indicated by dissolved-solids and trace-element content, generally is of suitable chemical quality for most purposes but is not without some problems. Dissolved-solids concentrations ranged from an average of less than 500 mg/L

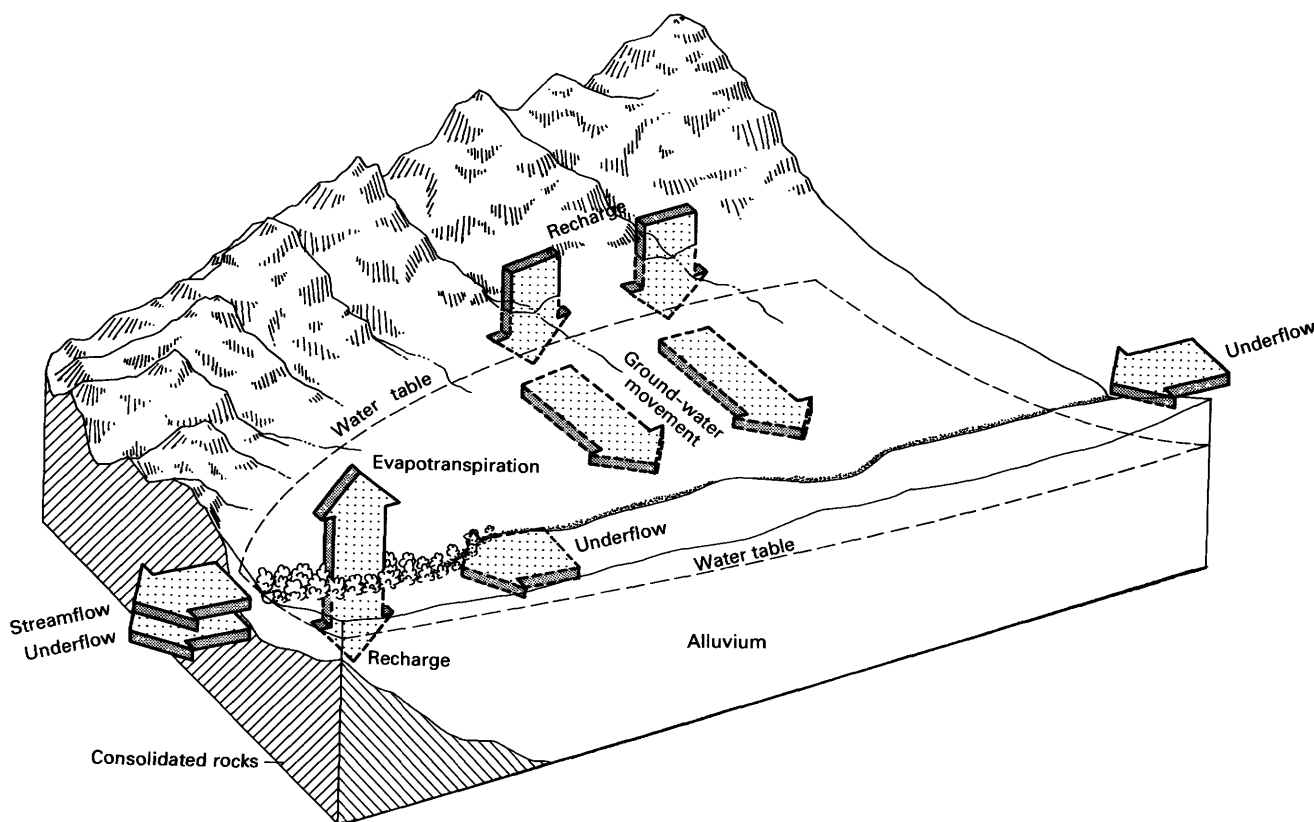


FIGURE 6.—Recharge, movement, and discharge of ground water.

(milligrams per liter) in 11 of the 28 basins sampled during this study to more than 3,000 mg/L in basins along the Gila and Colorado Rivers (see section entitled "Chemical Evolution of the Ground Water"). Ground water in most of the basins sampled contained concentrations of less than 1,000 mg/L. Ground water in most of the 72 basins generally contains average concentrations of less than 1,000 mg/L (Kister, 1973). The ground water in most basins can be classified (Durfor and Becker, 1964) as hard ( $>120$  mg/L) to very hard ( $>180$  mg/L). The average hardness of the ground water sampled was 314 mg/L as calcium carbonate and ranged from a low of 35 mg/L in lower San Pedro Valley to a high of 629 mg/L in West Salt River Valley. In several basins, the ground water contains large concentrations of the trace elements—fluorine, chromium, arsenic, lead, boron, or selenium—that exceed standards established for public supply or certain agricultural uses.

#### SOURCES OF DISSOLVED SPECIES

##### CALCIUM

Calcium, as well as the other alkaline earths, ionizes readily and forms a considerable number of moderately

soluble compounds such as carbonates, fluoride, hydroxides, and phosphates. Its ionic radius of 0.99 Å (angstrom) allows calcium to enter into eightfold coordination with tectosilicates, producing stable structures with both ferromagnesian and nonferromagnesian minerals. Weathering of plagioclase and dissolution of calcite and probably dolomite are widespread sources of calcium in all basins. The ferromagnesian minerals of the pyroxene and amphibole groups also are minor sources. Gypsum and anhydrite, although not as widespread, are the most prolific sources where they occur in playas or evaporites.

##### MAGNESIUM

Magnesium, also an alkaline earth, behaves geochemically differently from calcium. Because of its smaller ionic radius, 0.66 Å, magnesium occurs mainly in sixfold coordination and is not found in feldspars but is incorporated in ferromagnesian minerals during early crystallization of magmas. Thus, in primary rock genesis, magnesium resembles iron or manganese more than calcium (Rankama and Sahama, 1950). Silicate sources of magnesium are the ferromagnesian minerals augite, hornblende, and biotite. Dolomite, if present, may be a major source of magnesium.

## SODIUM

Sodium, together with lithium, potassium, rubidium, and cesium, is part of the alkali metal group. Sodium compounds are highly water soluble because the large ionic size and monovalent charge decrease the attractive forces within the crystal below those of the water dipoles. The ionic radius of sodium, 0.98 Å, is close to that of calcium, and therefore sodium is also found with calcium in eightfold coordination in silicate minerals. Because of its smaller charge, however, sodium does not tend to be incorporated in the higher temperature ferromagnesian minerals. The most widespread source of sodium is the weathering of feldspars. Halite (NaCl), where present in the basin fill, can cause large concentrations of solute sodium.

## POTASSIUM

Potassium, because of its larger ionic radius, 1.33 Å, and its correspondingly high coordination number of 8 to 12, forms minerals that are the last to crystallize from cooling magmas. Potassium feldspar is formed near the final stages of crystallization and is the major source of potassium. Micas and feldspathoids also contain potassium and may be additional sources. Although potassium is nearly as abundant as sodium in the rocks, unlike sodium, it is present in ground water only in small concentrations.

## CHLORIDE

Chlorine is a member of the halogen family, a highly electronegative group that forms monovalent ionic compounds or salts. Chloride, the ionized form, is enriched in the last fraction of cooling magmatic liquids and vapors; consequently, alkali rocks, pegmatites, volcanic emanations, and hydrothermal solutions are characterized by large concentrations of chloride (Rankama and Sahama, 1950). Ore deposits or hydrothermal deposits are sources of chloride in most basins. Chloride in precipitation and chloride in airborne particles probably are insignificant sources. Owing to the high solubility of most chloride compounds, particularly halite, the compounds are concentrated in evaporites or playa deposits. Deposits of halite, whether they predate the basins or were formed during basin deposition, if present, are the source of all large chloride concentrations.

## SULFATE

Sulfur has properties of a nonmetal and forms binary covalent compounds with metals and oxides with oxygen. Sulfur occurs in the elemental state and in oxidation states of -2 to +6 and can be divided into two general classes—the reduced form as sulfides and the oxidized

form as sulfates. In high-temperature volcanic and hydrothermal environments, sulfur is present as sulfides, but when exposed to the atmosphere or oxygenated water during weathering, the sulfides are oxidized to sulfates. The sulfates are moderately soluble and can be concentrated in evaporites and playa deposits as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or anhydrite ( $\text{CaSO}_4$ ). These deposits are the sources of the large sulfate concentrations found in some basins. Ore deposits or hydrothermal deposits probably are sources of sulfate in most basins.

## CARBON

Carbon is a nonmetal which, through sharing of the four electrons in its outer shell, forms strong covalent bonds and exists in oxidation states of -4, 0, and +4. It occurs in the reduced form as methane and organic carbon and in the oxidized form as carbon dioxide. Carbon dioxide is the stable form in the study area, where it occurs primarily as the bicarbonate ion, which is the dominant ion in dilute waters. The principal source of carbon is soil-gas carbon dioxide produced by respiration of plants. Paleozoic carbonate rocks, which occur locally, may be additional sources. The parameters of total inorganic carbon ( $C_T$ ), which is the summation of all dissolved carbon species in solution, and of the partial pressure of carbon dioxide ( $P_{\text{CO}_2}$ ) are calculated using field-measured pH, temperature, and alkalinity.

## SILICA

Silicon is a metalloid showing properties of both metals and nonmetals. The metalloid nature is observed in the silicon-oxygen bond, as it is neither ionic nor covalent but intermediate in nature. Silicon unites with oxygen and forms stable silica tetrahedra consisting of four oxygen atoms about a silicon atom. These tetrahedra may exist as separate units or may join in single or double groups, chains, or sheets to form an enormously large family of generally insoluble silicate minerals. Plagioclase followed by potassium feldspar and the ferromagnesian silicate minerals are the major sources of dissolved silica in the ground water. Quartz, because of its low solubility, and volcanic glass, because of a general paucity in the basin fill, are not major sources.

## GEOCHEMICAL ENVIRONMENT

The functional relation between the geologic environment and the stability of minerals has profound influence on the coexisting chemical composition of the water. To provide critical information on weathering sequences and stability of minerals, the ability of the hydrochemical system to oxidize or reduce an element—commonly called the redox potential, or Eh—must be estimated,

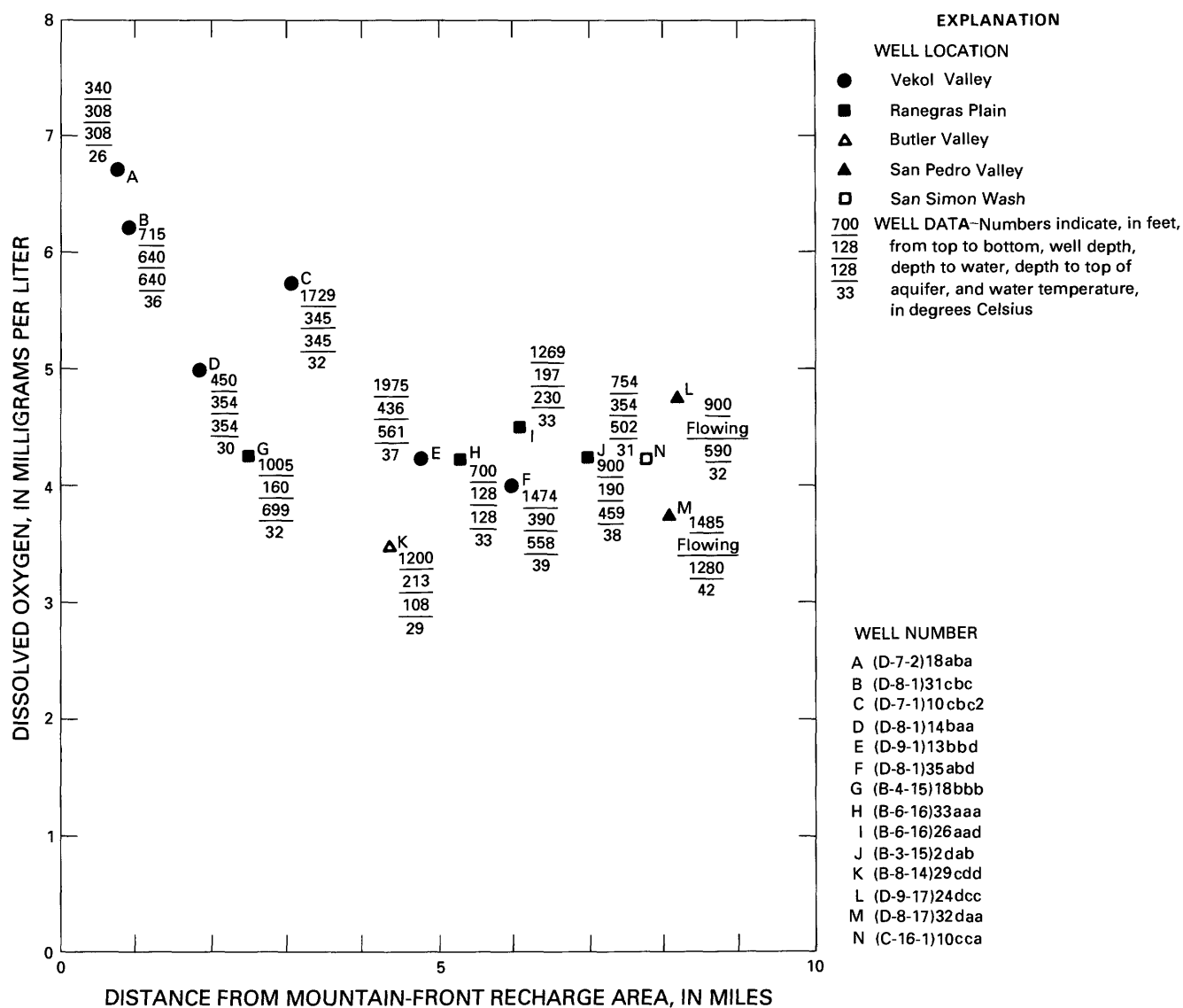


FIGURE 7.—Dissolved-oxygen concentrations and distance along flow paths for selected basins.

computed, or measured. The redox potential, expressed in volts or  $p_e$ , represents the chemical behavior of a redox couple with respect to known oxidizing or reducing agents. The geochemical environment of an aquifer in relation to the weathering of rocks and the formation of secondary minerals, and to the subsequent solute chemistry, is a function of the redox potential and the hydrogen ion concentration or pH of the system.

#### DISSOLVED OXYGEN

Oxidizing environments were confirmed throughout the study area. Field determinations of dissolved oxygen at the wellhead revealed that significant concentrations (>3 mg/L) of dissolved oxygen are present in ground water in all the alluvial basins, regardless of geologic

setting or location of wells within a basin. Dissolved oxygen was detected in water from wells nearly 2,000 ft deep and in waters that are older than 10,000 years as indicated by hydraulic and  $^{14}\text{C}$  data. Dissolved-oxygen concentrations for several basins plotted as a function of distance along a flow path are shown in figure 7. The distance along the flow path generally was defined as the distance from the nearest major mountain front, which presumably receives the greatest precipitation, to the well. Well C may be an exception, as it apparently receives some recharge along lower Vekol Wash. Most of the basins sampled are agriculturally undeveloped and generally are overlain by a confining layer.

The deepest well sampled, 1,975 ft, is in Vekol Valley. The basin-fill sequence is described in the section on Vekol Valley. Twelve-inch steel casing is perforated

between 603 and 1,973 ft. A depth to water of 436 ft, the presence of a thick confining layer, and the lack of ponding conditions preclude percolation of overlying oxygen-rich water. The distance to the recharge area is about 8 or 9 mi, assuming that recharge along the Sand Tank Mountains supplies the major recharge to the basin (Wilson, 1979). This assumption is probably valid owing to the greater precipitation that falls on these mountains. The dissolved-oxygen concentration of the ground water is about 70 percent of saturation.

The validity of the sampling and analytical techniques is best demonstrated by the 1,485-ft-deep flowing well in lower San Pedro Valley that taps the regional confined aquifer. The aquifer is situated approximately at the 1,370- to 1,485-ft interval and may be overlain by as much as 1,200 ft of gypsiferous clay and silt. The confining layer, the current hydraulic heads of about 20 ft above the land surface, and the flow rates on the order of 50 to 75 gal/min preclude mixing of recent recharge with water in the confined aquifer.

The sample bottles were suspended down the well casing, purged, and sealed under water, precluding any atmospheric contamination during sampling. Purge tests involving introduction of dye into the sample bottle prior to filling indicated that within 20 minutes the flowing water completely purged the bottle. A Hack model OX-2P field kit was used for the analyses, which were verified at other sites by a YSI model 57 dissolved-oxygen meter. Identical values of 3.75 mg/L for five replicates attest to the validity of the sampling and analytical methods.

#### TOTAL ORGANIC CARBON

The total organic carbon content of the ground water is small. The content in 13 of 31 samples analyzed was below the detection limit of 0.1 mg/L. The concentrations in the remaining 18 samples ranged from 0.1 to 2.7 mg/L, and the average and median values were 0.68 and 0.4 mg/L, respectively. Contamination by pump lubricating oil is suspected in many cases to be the cause of the higher values. Oil was observed frequently on the 0.45- or 0.10- $\mu$ m (micrometer) pore-size filters. The small concentrations of total organic carbon are consistent with the oxygenated waters.

#### DEPOSITIONAL ENVIRONMENT

The oxygenated ground water can be explained by the depositional history and hydrology of a basin. The basin-fill sediments were transported into the basin and deposited under oxidizing conditions. Presumably, the detritus remained in an oxidized state during burial either above or below the water table. The absence of carbon or

sulfide minerals in drill cores attests to the oxidizing environment. The oxidized sediments also indicate that deposition was not accompanied by the existence of perennial lakes, which are characterized by reducing conditions. Ponding conditions, if present, were probably limited to shallow oxygenated ephemeral lakes or playas. Surface runoff saturated with dissolved oxygen before infiltration remains oxygenated because little organic matter is available in the sediments.

#### SOLUBILITY EFFECTS OF OXYGENATED ENVIRONMENTS

The oxidizing nature of the alluvial aquifers is noteworthy and geochemically significant (Winograd and Robertson, 1982) because most of the literature depicts ground water as basically reducing. Solubility and movement of many elements are dependent on the redox potential of the ground water. In the relatively narrow pH range of 7–9, a small change of the redox potential may mobilize metals. The mobilities of arsenic, chromium, molybdenum, nitrogen, sulfur, selenium, vanadium, and uranium are greatly increased by oxidizing conditions if converted to the oxyanion form in their highest oxidation state. Iron and manganese, on the other hand, form insoluble metal oxides and are immobile in their higher oxidation states but become soluble in their lower states under reducing conditions.

#### OCCURRENCE AND DISTRIBUTION OF MINOR AND TRACE ELEMENTS

Ground water in selected basins was routinely sampled and analyzed for aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, mercury, molybdenum, selenium, strontium, uranium, vanadium, and zinc. The mean, standard deviation, and range of concentrations of these elements are shown in table 1. Because of the oxidizing nature of the ground water and the composition and texture of the alluvium, concentrations of several of these elements are larger than would be expected in these ground-water systems and in many samples exceed maximum contaminant levels for drinking water established by the U.S. Environmental Protection Agency (1977). Fluoride, chromium, arsenic, nitrate, and boron, in particular, present environmental problems in several basins.

#### FLUORIDE

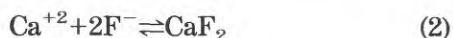
Fluoride is widely distributed in the ground water in the study area. The maximum contaminant level for fluoride is between 1.4 and 1.8 mg/L and is based on annual average maximum daily air temperatures ranging



from 45 to 90 °F. Twenty-five percent of the 546 samples analyzed exceeded 1.8 mg/L. Because of the prevalence of large fluoride concentrations that exceed the maximum contaminant level, obtaining potable ground water for public supply is a major problem in many basins. The occurrence and variability of fluoride appears to be related to several controls: (1) mineral-equilibrium reactions, (2) sorption or desorption reactions, and (3) availability of the fluoride ion in the rocks.

During the rock-forming process, the fluoride ion generally is concentrated in residual fluids of cooling magmas, as evidenced by its occurrence in fumaroles, pneumatolytic and hydrothermal deposits, pegmatites, and volcanic glass (Goldschmidt, 1958). The acidic and intermediate volcanic rocks are a suspected major source of fluoride, as these types of rocks commonly are found throughout the study area and occur to some extent in most basins. In volcanic rocks, fluoride may reside in the glass phase as well as in the rock minerals. Fluoride in hornblende and micas is probably an additional source, as these minerals are found in most intrusive and metamorphic rocks.

Solute calcium may be a control of fluoride in ground water through equilibrium reactions with the mineral fluorite. Fluorite is thought to be a control of fluoride in basins that contain concentrations greater than ~5 mg/L. Under equilibrium conditions, small concentrations of calcium permit large fluoride concentrations in solution:



or

$$[\text{Ca}^{+2}] [\text{F}^{-}]^2 = K_{\text{sp}}, \quad (3)$$

where

Ca = calcium,

F = fluoride,

CaF<sub>2</sub> = fluorite,

K<sub>sp</sub> = solubility product, and

[ ] represent thermodynamic activity.

Concentrations of less than ~5 mg/L do not appear to be controlled by equilibrium with fluorite or other minerals (Robertson, 1986).

A strong correlation of fluoride with pH significant at the 0.01 percent level ( $p < 0.0001$ ) indicates that pH-dependent exchange or sorption reactions are important controls of fluoride concentrations. During weathering of rocks and release of fluoride ions into solution, the ions may initially exchange for hydroxyl groups on montmorillonitic clays. As pH increases downgradient, greater concentrations of hydroxyl ions may effect an exchange of hydroxyl for fluoride ions, thereby increasing the concentrations of fluoride. An assumption of pH-dependent exchange of fluoride solely on the basis of the

pH-fluoride correlation may be tenuous, however, because the correlation is assumed not to be an indirect effect of other reactions, specifically pH increases and calcium decreases downgradient. The assumption is strengthened by a weaker calcium-fluoride correlation and the fluorite saturation data. A much stronger correlation coefficient of pH and fluoride compared with that of calcium and fluoride ( $p < 0.001$ ) and the fact that the correlation occurs in ground waters that are undersaturated with respect to fluorite support a direct effect of hydroxyl-fluoride exchange.

Leachate analyses of basin-fill sediments also indicate that sorption-desorption is occurring. Analyses show that leachable fluoride is present in amounts generally twentyfold more than concentrations found in the ground water and thus is available for dissolution to the aqueous phase. Because the solubility product of fluorite is not reached in the ground water of most basins, exchange or sorption-desorption reactions appear to be a major control (Robertson, 1984).

#### CHROMIUM

Chromium in the +6 oxidation state, or hexavalent state (Cr<sup>+6</sup>), is a naturally occurring constituent in the ground water throughout much of central and western Arizona (fig. 8). Five percent of 436 samples contained Cr<sup>+6</sup> concentrations above the maximum contaminant level of 50 µg/L (micrograms per liter). Large concentrations of Cr<sup>+6</sup> may be more prevalent than indicated by

TABLE 1.—Mean, standard deviation, and concentration range of selected trace and minor elements in ground water  
[In micrograms per liter]

Element	Number of samples	Mean	Standard deviation	Range
Aluminum .....	363	9.8	20.1	0-300
Arsenic .....	467	15.7	31.6	0-1,300
Barium .....	314	95.9	464.7	0-8,100
Beryllium .....	296	00.0	00.0	0-2
Boron .....	453	539.8	905.4	7-11,000
Cadmium .....	336	00.0	00.0	0-2
Chromium .....	436	10.3	30.7	0-300
Cobalt .....	298	.1	.7	0-6
Copper .....	369	2.3	7.4	0-70
Iron .....	485	19.2	59.2	0-810
Lead .....	371	3.1	10.9	0-110
Lithium .....	295	136.2	221.1	7-2,600
Manganese .....	494	6.0	40.2	0-720
Mercury .....	387	0.1	0.2	0-0.2
Molybdenum .....	347	7.7	16.6	0-150
Selenium .....	434	1.9	3.1	0-30
Strontium .....	311	1,590.6	2,481.3	0-2,100
Uranium .....	30	10.3	7.3	1.2-27
Vanadium .....	293	18.5	19.0	0-130
Zinc .....	379	57.5	189.7	0-2,900

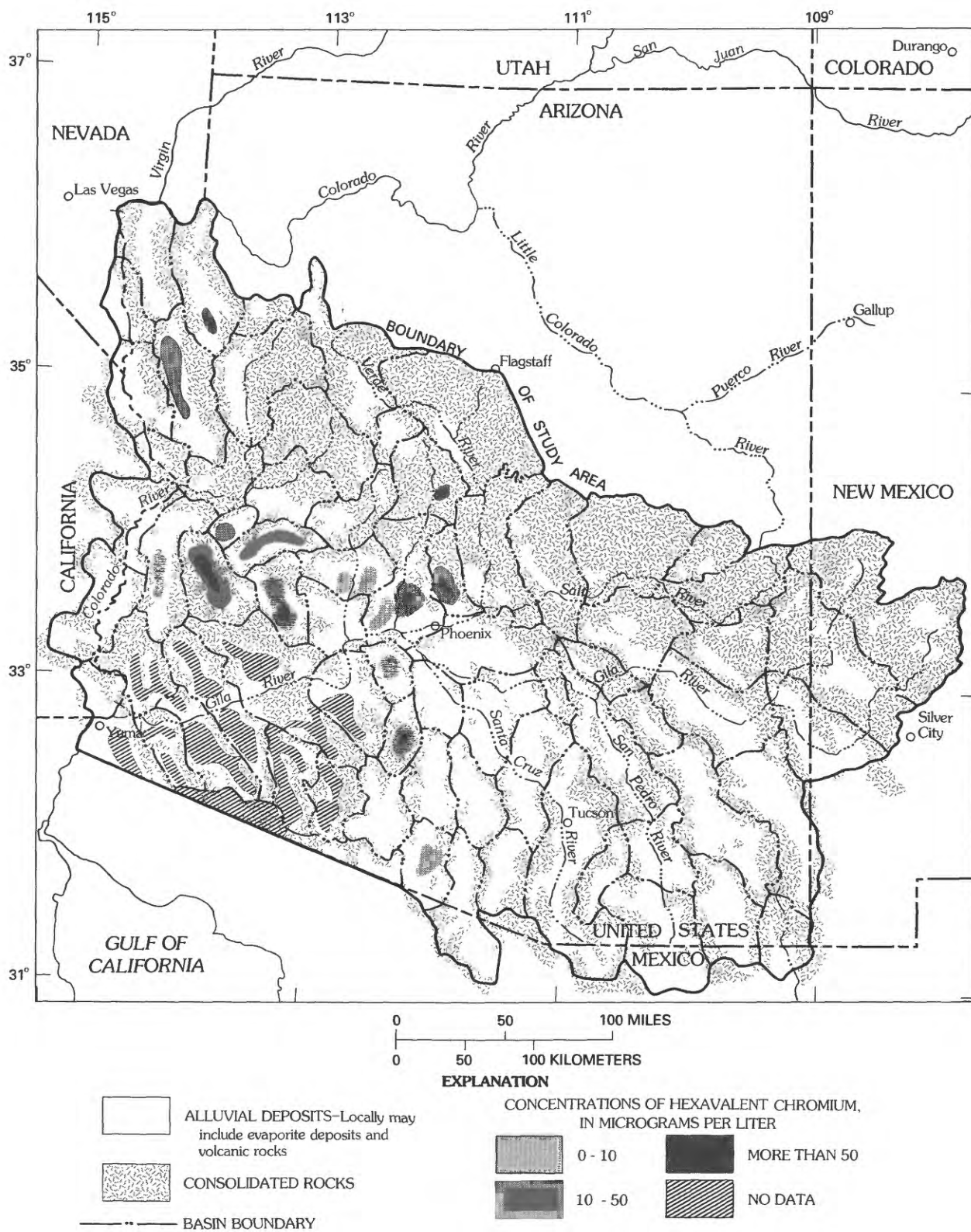
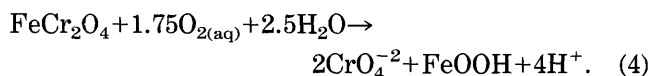


FIGURE 8.—Occurrence and distribution of hexavalent chromium.



the sampling program, however, because a relatively large part of western Arizona is undeveloped and all areas could not be evaluated.

The source of  $\text{Cr}^{+6}$  is the trivalent chromium ( $\text{Cr}^{+3}$ ) in the basin fill. Chromium is one of the most widely dispersed elements and occurs in rocks of all principal types (Ahrens, 1965). Chromium occurs primarily in the mineral chromite ( $\text{FeCr}_2\text{O}_4$ ), the economic source of chromium, and in silicate minerals of clinopyroxenes, amphiboles, and micas as replacement of ferric iron. Trivalent chromium is the normal form in the weathering environment and is highly insoluble and immobile, but under oxidizing and existing pH conditions, it may be oxidized to  $\text{Cr}^{+6}$  and form the soluble chromate ion ( $\text{CrO}_4^{-2}$ ). The dissolved oxygen probably is the oxidant of the  $\text{Cr}^{+3}$ . The oxidation of the mineral chromite in an oxygenated environment may proceed by



The presence of  $\text{Cr}^{+6}$  in the ground water is closely related to the geology, hydrology, and geochemical environment of the aquifer. Occurrence and magnitude are associated with source rock type and with areas in basins that contain ground water that is old, oxidizing, and high in pH. Larger  $\text{Cr}^{+6}$  concentrations, those greater than 50  $\mu\text{g/L}$ , occur most commonly in basins bounded by volcanic rocks, particularly intermediate volcanic rocks.  $\text{Cr}^{+6}$  is also found in ground water of basins bounded by intrusive rocks, but concentrations there generally are smaller (Robertson, 1984). The basins that contain the largest concentrations are those that receive the least recharge, resulting in ground water having long residence time. Concentrations of  $\text{Cr}^{+6}$  range from 0  $\mu\text{g/L}$  in lower San Pedro Valley and other basins in the eastern part of the study area to 60  $\mu\text{g/L}$  in Vekol Valley and 300  $\mu\text{g/L}$  in Ranegras Plain.  $\text{Cr}^{+6}$  does not occur in the ground water in the eastern part of the study area where precipitation and recharge are significantly higher.

$\text{Cr}^{+6}$  correlates positively ( $p < 0.0001$ ) within the study area with pH, fluoride, vanadium, and uranium. Correlation with fluoride may be an indirect effect of a pH-fluoride-dependent exchange control. The correlation with vanadium and uranium may be due to their geochemical similarity; vanadium and uranium, like chromium, are oxidized to their highest, most soluble oxidation state.

The oxidation of  $\text{Cr}^{+3}$  is a pH-dependent reaction and is favored by high pH conditions. High pH conditions occur basinward as a result of silicate hydrolysis, which, under closed hydrochemical conditions, proceeds more rapidly than solution  $\text{CO}_2$  uptake or availability. Conditions for  $\text{CO}_2$  removal are optimal under high reaction

rates associated with hydrolysis of intermediate volcanic and pyroclastic rocks (Jones, 1966) and probably account for the larger  $\text{Cr}^{+6}$  concentrations associated with rocks of these types. The reactions and concomitant increases in pH are reflected in the distribution of  $\text{Cr}^{+6}$  where the distribution is characterized by small concentrations near the basin margin that increase basinward to a maximum near the basin center (Robertson, 1984).

Because chromium solubility is related to the pH and the redox potential of the ground water, the solubility of chromium species was examined thermodynamically by Eh-pH measurements using the equipment of Back and Barnes (1961). Although Eh measurements are quantitatively questionable, as the solubilities derived from them do not always agree with theoretical values derived from the Nernst equation, the measurements proved useful in describing the oxidizing environment and explaining the  $\text{Cr}^{+6}$  occurrences. The occurrences are concluded to be a result of oxidation of the  $\text{Cr}^{+3}$  within the basin fill, as the measured potentials using a platinum electrode and the pH values give equilibrium solubilities close to those observed. The  $\text{Cr}^{+6}$  appears to be in equilibrium with  $\text{Cr}^{+3}$  oxyhydroxide. Thus, the  $\text{Cr}^{+3}$  species is the electron donor in the half-cell reaction. The oxidation may be unique in the sense that, assuming that the electrode is not responding to dissolved oxygen and that other redox-controlling couples are absent, the electrode may be responding to the unique  $\text{Cr}^{+3}$ - $\text{Cr}^{+6}$  couple. Calculated equilibrium solubilities of  $\text{Cr}^{+3}$  in the ground water under existing pH and redox conditions should be on the order of  $10^{-7}$  to  $10^{-8}$  M (molar), and the observed  $\text{Cr}^{+6}$  concentrations are on the order of  $10^{-5}$  to  $10^{-6}$  M. Reliable measured potentials may be possible in the  $10^{-5}$  to  $10^{-6}$  M concentration range (Stumm and Morgan, 1981, p. 491) under favorable conditions, particularly in the absence of other redox couples or mixed potentials. The existence of a disequilibrium system (Thorstenson, 1984) involving iron or manganese—and probably other redox couples—may not be critical because reactions involving these elements may have gone to completion. As discussed later, model results show that minerals containing iron and manganese weather increasingly slower or not at all downgradient, thus diminishing the importance of kinetic reactions at the electrode. The absence of interfering redox potentials could readily explain the large concentrations of  $\text{Cr}^{+6}$  in older waters and the absence of  $\text{Cr}^{+6}$  in younger waters. Because Eh measurements were made in only two basins during the study, it is not known if the measurements are predictive throughout the area. On the basis of the few measurements, the  $\text{Cr}^{+6}$  concentrations appear to be strictly a function of partial heterogeneous equilibrium of the ground water with the trivalent chromium solid.

## ARSENIC

Nearly 7 percent of the 467 samples analyzed for arsenic exceeded the maximum contaminant level of 50  $\mu\text{g/L}$ . Notably large arsenic concentrations were found in ground water in Verde Valley and on the Papago Indian Reservation in south-central Arizona. Concentrations exceeded 200  $\mu\text{g/L}$  in both areas, and average concentrations were 59 and 62  $\mu\text{g/L}$ , respectively. Verde Hot Springs contained an arsenic concentration of 1,300  $\mu\text{g/L}$ .

All five outer shell electrons of the arsenic atom participate in the formation of compounds, and, consequently, arsenic occurs in oxidation states ranging from  $\text{As}^{-2}$  to  $\text{As}^{+5}$ . The most common compounds of arsenic are the sulfides in the reduced form and arsenates in the oxidized form. The numerous oxides of arsenic form when sulfide and arsenide deposits are exposed to oxygen of the atmosphere or with oxygenated waters. The arsenates, arsenic as  $\text{As}^{+5}$ , are the predominant oxide minerals and the most stable species in oxygenated waters. Arsenic also occurs as arsenite ( $\text{As}^{+3}$ ) in mildly reducing waters (Hem, 1985). Arsenic speciation of several samples from the reservation confirmed that arsenic occurs as  $\text{As}^{+5}$ .

The source of the arsenic in the ground water is oxidized arsenic compounds in the basin fill, which are suspected to be derived from hydrothermal sulfide and arsenide deposits in the surrounding mountains. Arsenic presumably is oxidized to  $\text{As}^{+5}$  before transport into the basin or, if after transport, before burial. The occurrences of arsenic, probably in the arsenate form  $\text{HAsO}_4^{-2}$ , and the circumstances of its removal are related to several factors—the oxidation state of the arsenic, the Eh and pH of the water, and the nature of the surface (soil and sediment) that adsorbs or immobilizes arsenic. In oxidizing environments,  $\text{As}^{+5}$  is strongly retained on fine and medium sands relative to  $\text{As}^{+3}$ ; the retention may be related to the interaction between  $\text{As}^{+5}$  and  $\text{Fe}^{+3}$  (Ferguson and Davis, 1972; Gulens and others, 1979). Consequently, arsenic is enriched in the basin-fill sediments relative to its crustal abundance of about 2 ppm (parts per million). The arsenic content of samples of basin fill analyzed ranged between 2 and 88 ppm. The highest arsenic values were found in Verde Valley—7 to 88 ppm—from well cuttings and outcrop samples of the Verde Formation of Miocene and Pliocene age. The lower values were found in clean limestones, and the higher values in clayey limestones and red clay beds near Lake Montezuma (Owen-Joyce and Bell, 1983; Robertson, 1986).

Arsenic in the ground water correlates most strongly ( $p < 0.01$ ) with lead, molybdenum, selenium, vanadium, and fluoride. Except for lead and fluoride, all elements occur as negative oxyanions like arsenate. Fluoride,

although not an oxyanion, also is a negative ion. Although arsenic shows no significant correlation with dissolved iron (correlation coefficient,  $r = 0.09$ ), arsenic concentrations and arsenic removal appear to be controlled partly by iron in the solid phase. Water from the village well at Pisinimo on the Papago Indian Reservation contained, at different times, arsenic concentrations between 0 and 50  $\mu\text{g/L}$  and concentrations exceeding 100  $\mu\text{g/L}$ . A time-series analysis indicated that the arsenic concentrations were directly related to the pumping time, to the redox potential, and to the dissolved-oxygen content and inversely related to the iron concentrations in the ground water. The well, after sitting idle for a period of weeks, initially produced water high in iron and low in arsenic and dissolved oxygen.

Coprecipitation or adsorption of the arsenate ion on ferric hydroxide (or ferric oxyhydroxide) was considered the simplest and most plausible mechanism for the removal of arsenic from solution. The pH of the ground water (8.2) remained constant throughout the test, which, along with the trend in dissolved oxygen, suggests that Eh is a significant factor (Robertson, 1986).

Mineralogic controls appear to have little or no effect on arsenic solubility in the oxygenated environment. Speciation and saturation data show the ground water to be very highly undersaturated with respect to the arsenate and arsenite minerals  $\text{As}_2\text{O}_5$ ,  $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Pb}_3(\text{AsO}_4)_2$ ,  $\text{Zn}_3(\text{AsO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ , and  $\text{As}_2\text{O}_3$  (arsenolite and claudetite). Judging from the concentrations of arsenic and metals found in the ground water, it is unlikely that other metal-arsenic compounds are mineralogic controls of arsenic.

A major control of arsenic occurrence and removal appears to be the coprecipitation or adsorption of  $\text{HAsO}_4^{-2}$  on active ferric oxide or oxyhydroxide surfaces. The removal process would also explain the large arsenic concentrations found in the red clay beds near Lake Montezuma, in which the red color is due to the presence of ferric oxides (Robertson, 1986).

## BORON

Boron concentrations normally found in drinking water and food are not toxic to humans, but plants may be affected by small concentrations. Citrus trees are particularly sensitive to boron and may begin to show toxicity symptoms if the concentrations exceed 1,000  $\mu\text{g/L}$  (Gough and others, 1979). Boron concentrations in the ground water ranged from 7 to 11,000  $\mu\text{g/L}$ , and concentrations in about 13 percent of the samples exceeded 1,000  $\mu\text{g/L}$ . Boron concentrations tend to be lower in the southeastern basins and higher in the central and western basins, suggesting that aridity may play

some role. Average boron concentrations range from 40  $\mu\text{g/L}$  in the Willcox basin to 1,200  $\mu\text{g/L}$  in Ranegras Plain.

Boron is enriched in the residual portions of magmas and hydrothermal solutions and crystallizes as independent minerals only during the hydrothermal or pegmatite stage. The small ionic radius of trivalent boron, the only oxidation state, of 0.23 Å prevents its substitution in late-crystallizing hydroxyl-bearing minerals. Tourmaline is the most abundant of the boron silicate minerals. Boron replaces silicon in the tetrahedral structure, but the substitution is small because of considerable differences in the ionic radii of the two elements ( $\text{Si}=0.42$  Å). The total amount concealed in the silicate structure is geochemically significant, however, as the crustal abundance of boron is only about 5 ppm.

In addition to boron substitution in silicate tetrahedral minerals and a few late magmatic borosilicate minerals, boron is found in volcanic emanations. Boron from these emanations as soluble borate may form important economic deposits if it accumulates in closed basins as evaporites or playa deposits. The borate deposits in the playas of southern California and Nevada are the world's most abundant source of boron and contain the minerals kernite ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ), borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), ulexite ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ), and colemanite ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ) (Rankama and Sahama, 1950).

Boron correlates positively ( $p<0.0001$ ) with chloride, sulfate, dissolved solids, nitrate, and molybdenum. The positive correlations of boron with generally soluble constituents suggest that evaporites in the basin fill are sources of the large concentrations of boron in the ground water. The large concentrations in Ranegras Plain probably are due to the presence of the evaporites in the lower basin fill. The boron in the evaporites may be hydrothermal in origin or may have resulted from weathering of borosilicate minerals, including the silicate tetrahedral minerals in the rocks surrounding the basin. The overall larger boron concentrations in the western basins may be a function of aridity through the reworking of the secondary boron compounds in the soil or unsaturated zone.

#### NITRATE

Nitrogen could be considered a major element but is included in this section with the minor and trace elements because of its environmental implications. About 12 percent of the 480 ground-water samples analyzed for nitrate exceeded the maximum contaminant level of 45 mg/L as nitrate. Average concentrations range from 0.5 mg/L in the basins along the Colorado River to 41.4 mg/L in West Salt River Valley. The sources of nitrogen are numerous and include natural aerosols, precipitation,

fixation by microorganisms, decaying organic matter, fertilizers, animal and industrial wastes, and weathering of consolidated and unconsolidated rocks. The nitrogen content of igneous rocks and sedimentary rocks as nitrate is about 46 and 510 ppm, respectively (Rankama and Sahama, 1950).

The large nitrate concentrations in West Salt River Valley have multiple sources. Hem (1970) cites an analysis of water from a well in an intensively irrigated and fertilized area in West Salt River Valley that contained a nitrate concentration of 83 mg/L, which probably is due, at least in part, to the leaching of fertilizers. In the north-central part of the valley, concentrations of more than 90 mg/L occur over a large area. A time-series analysis using historical data indicates that this high-nitrate area has been in existence at least since 1920 and possibly since the turn of the century (Schmidt, 1979). The spatial distribution of the concentrations and the time-series analysis indicate a natural or geologic origin of the nitrate. A thick, fine-grained unit of the upper basin fill that overlies the aquifer also supports a geologic origin. Nitrate occurrences of natural origin were also observed in the ground water of Vekol Valley, where concentrations ranged between 30 and 40 mg/L in the central part of the basin. Because the basin is undeveloped and the aquifer is overlain by a thick silt-clay unit, the concentrations are associated with a natural origin. Hem (1970) cites an analysis of water from a well 12 mi south of Gila Bend that contained a nitrate concentration of 68 mg/L. The large concentration probably was related to a natural source, as the area was undeveloped at the time of sampling.

Nitrate does not seem to have any controls other than the availability of nitrogen in the environment. Nitrate salts are highly soluble and, on the basis of leachate analyses discussed in the section on "Projection of Ground-Water Chemistry," do not sorb readily on the basin-fill sediments. Some natural sources of nitrogen in desert areas are rocks, animals, precipitation, atmospheric aerosols, dust, the legumes species of desert vegetation, caliche, and playa deposits (Feth, 1966). If precipitation were not sufficient to leach the soluble nitrate salts from soils—depositional rates exceed removal rates—an eventual increase in nitrate concentrations from these sources would occur in the ground water.

#### SELENIUM

About 2 percent of the 434 samples tested for selenium contained concentrations above the maximum contaminant level of 10  $\mu\text{g/L}$ . The geochemistry of selenium is similar to that of sulfur—also in group VI of the periodic table—but in some respects it is even more similar to

that of arsenic. Selenium occurs in four oxidation states, and its solubility is affected by redox potential, pH, and probably coprecipitation and sorption reactions. Under oxidizing conditions, selenium occurs as the selenite and selenate anions  $\text{SeO}_3^{-2}$  and  $\text{SeO}_4^{-2}$ , respectively, and under reducing conditions, as selenides,  $\text{Se}^{-2}$  (Lakin, 1972). The soluble species of selenium in ground water are the selenite and selenate forms (Hem, 1985).

Selenium correlates positively ( $p < 0.01$ ) with the elements arsenic, boron, calcium, chloride, magnesium, potassium, dissolved solids, sodium, nitrate, strontium, and sulfate and negatively with pH. The correlations of selenium with mostly soluble components may be explained by the higher solubility of the oxidized anion forms, and, like boron and nitrate, its occurrence can be associated with evaporites or playa deposits. A strong negative correlation with pH tends to discount Eh-pH-dependent mineral phases as a control in the oxygenated environment.

Availability of selenium in the basin fill could be a control, judging from the small crustal distribution. The abundance of selenium in the Earth's crust and in igneous rocks is only about 0.09 and 0.05 ppm, respectively (Lakin, 1972). The correlation of selenium with arsenic and the strong correlations of selenium with fluoride, molybdenum, and arsenic in Verde Valley, where the highest selenium concentrations occurred, however, suggest that selenium analogous to arsenic may be controlled by sorption on ferric oxide surfaces. If the chemical behavior of selenium parallels that of arsenic, enrichment of selenium in the basin fill could occur, discounting the crustal distribution and favoring the control of the dissolved species by sorption reactions. Chemical analyses of the basin fill for selenium are not available to define the distribution in relation to the dissolved phase.

#### BARIUM

About 1 percent of the 314 samples analyzed for barium exceeded the maximum contaminant level of 1,000  $\mu\text{g/L}$ . Concentrations ranged from 0 to 8,100  $\mu\text{g/L}$ ; however, most values did not exceed 500  $\mu\text{g/L}$ . Barium does not correlate in the ground water with any other element ( $p < 0.05$ ). In several individual basins, however, barium correlates positively ( $p < 0.01$ ) with strontium, calcium, lithium, and potassium. Barium correlates most significantly and frequently with potassium, which, along with the correlations with the alkaline earths and lithium, indicates that potassium feldspar and possibly alkali basalt are the likely sources of barium.

Dissolved barium apparently is controlled by the solubility product of the highly insoluble mineral barite ( $\text{BaSO}_4$ ):



or

$$[\text{Ba}^{+2}] [\text{SO}_4^{-2}] = K_{\text{sp}} \text{ barite.} \quad (6)$$

Large amounts of barium, however, also are removed from solution by ion exchange or adsorption by secondary clay minerals. Barium is preferentially absorbed relative to sodium, calcium, strontium, and magnesium (Nesbitt and others, 1980). Although barium is preferentially retained, its occurrence in ground water nonetheless appears to be one of an inorganic solubility control. Saturation indices (defined in section entitled "Aqueous Speciation and Saturation Data") of barite for 12 basins range from 0.392 to  $-0.375$  and average  $-0.09$ , which indicates that the ground water is in equilibrium with respect to barite. The saturation data, the narrow concentration range of barium, and a poor correlation with sulfate, discounting gypsum or anhydrite as sources, indicate that mineral equilibrium is the sole control of barium (Robertson, 1984).

#### CHARACTERIZATION OF GROUND WATER IN RECHARGE AND DISCHARGE AREAS

The water chemistry of the recharge areas and the downgradient areas is summarized in table 2. In the recharge areas, the ground water is typically a calcium bicarbonate type. Recharge areas generally contain large concentrations of bicarbonate ( $\sim 5.0$  mmol/L (millimole per liter)) and calcium ( $\sim 2.0$  mmol/L) and relatively small concentrations of magnesium, sodium, chloride, sulfate, and fluoride (all  $< 1.0$  mmol/L). Chloride and sulfate concentrations are variable, but in general the lowest concentrations are found in the recharge areas. Ground-water temperatures generally range between 15 and 30 °C. The pH of the ground water generally is near neutral (6.9–7.4), and dissolved oxygen is always present and near saturation ( $\sim 9$  mg/L). Sulfide species, ferrous iron, organic carbon, and other reducing agents are absent. Concentrations of trace elements are small, commonly below detection limits.

In the downgradient areas, the composition evolves into either a sodium bicarbonate or sodium mixed-anion type or, as dissolved solids increase, into a sodium chloride or sodium calcium sulfate type. Total inorganic carbon,  $\text{P}_{\text{CO}_2}$ , and, in basins containing the more dilute waters, calcium and magnesium decrease markedly. Sulfate and chloride concentrations and, in some cases, calcium and magnesium increase depending on the availability of gypsum and halite within the basin fill. Temperatures increase to as high as 45 °C, and pH values increase to as high as 9.5. Dissolved oxygen is invariably present in concentrations typically ranging from 50 to 80

TABLE 2.—Analytical data for selected wells in recharge and downgradient areas

[In millimoles per liter unless otherwise indicated; values in parentheses are in milligrams per liter; meq/L, milliequivalents per liter. Dashes indicate no value was calculated]

	Recharge area (7 basins)			Downgradient area (23 basins)		
	Number of wells	Mean	Standard deviation	Number of wells	Mean	Standard deviation
pH (units) .....	9	7.21	0.20	547	7.61	0.46
Temperature (°C).....	9	25.8	3.80	521	27.130	5.29
Ca <sup>+2</sup> .....	13	1.948 (78)	.45 (18)	556	1.986 (80)	2.39 (96)
Mg <sup>+2</sup> .....	13	.590 (14)	.29 (7)	555	1.118 (27)	1.52 (37)
Na <sup>+</sup> .....	13	.970 (22)	.69 (16)	554	8.025 (185)	9.30 (214)
K <sup>+</sup> .....	8	.052 (1.9)	.02 (.8)	543	.125 (4.9)	.08 (3.0)
Cl <sup>-</sup> .....	13	.567 (20)	.45 (16)	554	6.921 (245)	10.45 (371)
SO <sub>4</sub> <sup>-2</sup> .....	13	.216 (21)	.19 (18)	501	2.040 (196)	3.36 (323)
Alkalinity (meq/L) .....	13	4.810 (294)	.67 (41)	554	3.407 (208)	1.80 (111)
F <sup>-</sup> .....	11	.013 (0.26)	.01 (.2)	546	.080 (1.5)	.10 (1.9)
NO <sub>3</sub> <sup>-</sup> .....	8	.490 (30)	.65 (40)	544	.457 (28)	.74 (46)
SiO <sub>2</sub> .....	11	.720 (44)	.10 (6)	554	.525 (32)	.20 (12)
Dissolved solids.....	11	— (495)	— (68)	554	— (938)	— (949)
*CO <sub>2</sub> .....	9	.60	—	521	<.10	—

\*Calculated.

percent of saturation, and concentrations of several trace elements increase basinward. Total dissolved solids of ~400 mg/L in the recharge area may decrease to less than 200 mg/L downgradient owing to precipitation reactions or may increase to several thousand milligrams per liter owing to dissolution reactions.

#### VARIATION WITH DEPTH

The dissolved-solids concentration in the ground water in some alluvial aquifers, roughly the upper 2,000 ft, may show slight increases or decreases with depth, but the trends are not statistically significant ( $p < 0.05$ ). Although data and well control are not complete in all basins, the following trends were observed: increasing dissolved-solids content with depth in Ranegras Plain, Verde Valley, and the Big Sandy and upper Santa Cruz basins and in the artesian aquifer in lower San Pedro Valley, and decreasing dissolved-solids content with depth in East and West Salt River Valleys, Harquahala Plain, Rainbow, McMullen, Hualapai, Sacramento, and Altar Valleys, and the Willcox basin, and in the water-table aquifer along the San Pedro River. In most of these basins, concentrations of magnesium, bicarbonate, and silica decrease with depth and pH, temperature, and the majority of trace elements increase with depth. Calcium generally, but not invariably, also decreases with depth.

The extent of mixing of waters within the aquifers is not known, but the chemistry of waters in the recharge and discharge areas suggests that vertical variations are less important than areal variations. The variation in the water chemistry within basins appears to be a function

more of the flow path than of mixing. The saturation state of the ground water is supporting evidence, as close equilibrium with respect to several minerals, particularly calcite, fluorite, and barite, suggests little mixing of waters of vastly different compositions.

#### CHEMICAL MODELS

A goal of chemical modeling is to identify probable reactions responsible for the evolution of the ground water and any chemical changes that occur within the aquifer as a result of these reactions. In addition to identification of reactions, the mass transfer—the amounts of all pertinent minerals or gases that dissolve or precipitate in the course of these reactions—should be defined. Determination of the mass transfer is possible for a specified chemical system if the number of dissolved chemical constituents equals the number of phases selected for reactants and products. For example, in a simplified system showing weathering of rocks,

$$a(\text{unweathered rocks}) + b(\text{water}) = c(\text{clays}) + d(\text{dissolved species}), \quad (7)$$

it is possible in theory to solve for the reaction coefficients  $a$ ,  $b$ ,  $c$ , and  $d$ , which define the mass transfer of each respective phase. However, the number of possible mineral and gas phases normally far exceeds the number of constituents. The large number of possible phases necessitates the use of many likely candidates and the elimination of the less likely. In a comprehensive treatment of all reactant and product phases, a “best fit” model is developed. A best fit model is one whose

reactions are most compatible with observed changes in water chemistry and with rock minerals (Plummer and others, 1983).

For this study, the computer code BALANCE (Parkhurst and others, 1982) was used to facilitate the calculation of the reaction coefficients. A series of simultaneous equations using initial and final water compositions and selected mineral or gas phases define the changes in molality of each constituent along a flow path by determining reaction coefficients for the specified mineral stoichiometry or gas compositions. Mass-balance calculations are constrained by relations of conservation of mass and electrons and are defined by the equation (Parkhurst and others, 1982)

$$\sum_{p=1}^P \alpha_p b_{p,k} = m_{T,k(\text{final})} - m_{T,k(\text{initial})} = \Delta m_{T,k} \quad (8)$$

for each element  $k=1$  to  $J$ , where  $P$  is the number of total reactant and product phases in the net reaction,  $\alpha_p$  is the calculated net mass transfer of the  $p$ th phase,  $b_{p,k}$  denotes the stoichiometric coefficient of the  $k$ th element in the  $p$ th phase,  $m_{T,k}$  is the total molality of the  $k$ th element in solution, 1 is the total number of species, and  $J$  is the number of elements included in the calculation. The mass transfer is defined as the number of millimoles per kilogram  $\text{H}_2\text{O}$  of reactant or product phases that enter or leave the aqueous phase<sup>1</sup>. The values of  $m_T$  are obtained from the analytical data. If the number of phases equals the number of elements, a mass balance for the selected minerals and gases can be obtained by the simultaneous solution of  $k$  equations.

As redox reactions are involved in the reaction models, it is also necessary to conserve electrons. The redox state for a solution is defined as

$$RS = \sum_{i=1}^I m_i v_i, \quad (9)$$

where  $RS$  is the redox state of the solution,  $m_i$  is the molality of the  $i$ th aqueous species, and  $v_i$  is the operational valence of the  $i$ th species. The operational valence is a set of conventions to handle the oxidation states of the various elements in the reaction. Equations 8 and 9 define the mass transfer that occurs in the chemical system along the flow path. Although the reactions occur along the flow path, they are not based on hydraulic principles. The reaction models are not to be confused with solute-transport models, which are based on hydraulic principles. For a detailed discussion of mass-

transfer calculations, see Parkhurst and others (1982), Plummer and others (1983), and Plummer (1984).

The reactant and product phases used in the chemical models were selected on the basis of published mineralogical information or were postulated through analysis of several types of data: (1) XRD (X-ray diffraction) analysis of the basin fill, (2) XRF (X-ray fluorescence) analysis of the basin fill, (3) speciation and saturation data, and (4) mass balance and isotopic constraints. The selection of the proper phases is a critical aspect of chemical modeling and requires significant knowledge and understanding of the hydrologic system and of the chemistry and mineralogy of the aquifer. The methodology and criteria for the selection of the final phases is discussed in later sections.

#### MINERALOGY OF THE BASIN FILL

The composition of the ground water is determined by reactions of water with minerals present in the soil and basin fill; hence some knowledge of the mineralogy is required. Detailed information on the mineralogy is limited, as most previous hydrologic investigations did not address mineralogic studies. As part of this study, 169 samples of drill core or well cuttings of alluvium from 21 wells in seven basins were analyzed. One-hundred seven samples of the less than 62- $\mu\text{m}$  particle-size fraction were analyzed by XRD for bulk mineralogy and by XRF for bulk chemistry, and 62 samples of the less than 2- $\mu\text{m}$  fraction were analyzed by XRD for clay mineralogy.

Quartz, plagioclase, calcite, potassium feldspar, muscovite, and clay were the most common minerals in the bulk fraction. Pyroxenes and amphiboles were detected in a few samples, and dolomite was detected in a few samples from the unsaturated zone. The distribution of plagioclase, one of the most abundant minerals in the bulk fraction, is shown in figure 9.

Samples for the clay-mineralogy analysis were separated into less than 2- $\mu\text{m}$  fractions, mounted on slides, and analyzed using standard procedures (Dixon and Weed, 1977). Samples were scanned at a rate of  $2^\circ 2\theta$  per minute using copper  $K_\alpha$  with  $\lambda = 1.542 \text{ \AA}$  radiation. Patterns were made after each of the following procedures: (1) treated with magnesium solution for exchange-site saturation and air dried; (2) treated with ethylene glycol; and (3) treated with potassium solution for exchange-site saturation and heated at 110, 300, and 500  $^\circ\text{C}$ . Peaks of the patterns that moved from near 15 to 17  $\text{\AA}$  upon ethylene glycol treatment and to 10  $\text{\AA}$  upon heating were identified as smectite. Nominal 10  $\text{\AA}$  peaks that showed no variation upon heating were identified as mica. Invariant 7  $\text{\AA}$  peaks were identified as kaolinite.

<sup>1</sup> For brevity, the reaction coefficients are referred to simply as millimoles, or mmol.

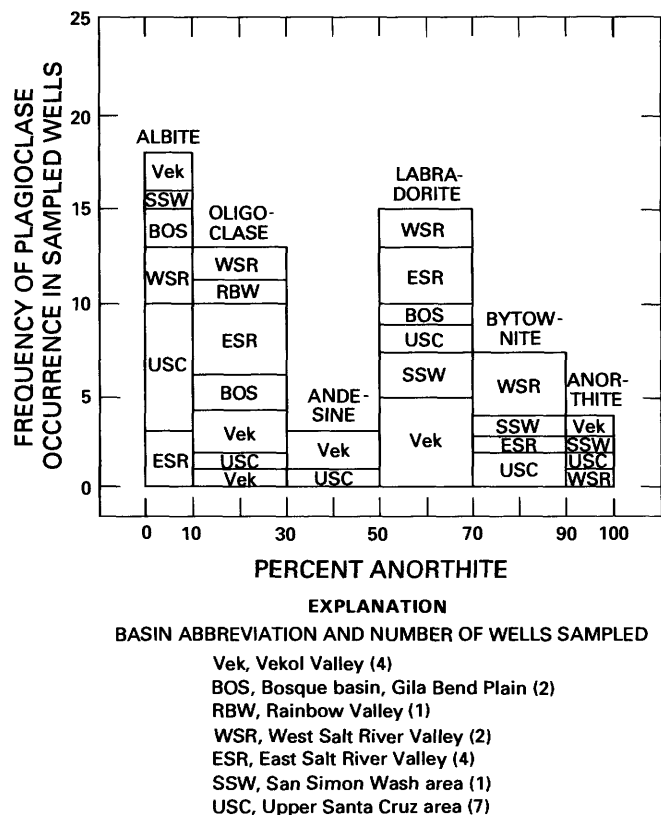


FIGURE 9.—Distribution of plagioclase for selected basins.

The results of the ethylene glycol treatment alone suggest that the samples are predominantly smectite or interstratified minerals with smectite layers. All patterns upon treatment show swelling to spacings near 17 Å that collapse to near 10.0 Å upon heating. The analysis also shows that the clay mineralogy of the basin fill is markedly uniform throughout the area and that along with smectite, trace to small amounts of muscovite and kaolinite are present. About 20 percent of the samples contained mixed layered clays, generally smectite interstratified with mica or vermiculite as components. Otherwise, vermiculite and chlorite are absent. The relative abundances of the clay minerals in the basin fill are indicated by the XRD patterns in figures 10, 11, and 12.

The clay mineralogy of the soil zone, less than 5 ft below land surface, also appears to be similar among basins in southern Arizona (U.S. Soil Conservation Service, 1974). Smectite generally is the dominant clay, but mica and kaolinite are commonly more abundant in soils than in the basin fill.

#### CHEMICAL ANALYSIS OF THE BASIN FILL

The chemical composition of the basin fill imposes an additional constraint on the selection and the composition of the mineral phases. The phases selected for the

modeling must agree with the chemistry as well as with the mineralogy of the respective source rocks because the chemical composition of the ground water is controlled in part by the chemical composition of the rocks in the soil, unsaturated, and saturated zones. Thus, selection of the correct mineral species also requires specification of the mineral stoichiometry, for which the chemical composition of the basin fill can establish limits. Caution must be exercised in interpreting chemical data singularly, however, as a combination of incorrect minerals may also have acceptable chemical compositions.

#### AQUEOUS SPECIATION AND SATURATION DATA

The selection of phases is based partly on the saturation state of the ground water with respect to the possible minerals, as the derived mass transfer must be consistent with thermodynamic or solubility constraints placed on the reactants and products. The derived minerals, dissolved or precipitated, should agree with those observed and those determined by the aqueous speciation.

The speciation of the solution supplies the activities and concentrations of the dissolved species, including some of those not analyzed, calculates the partial pressure of several gases, and determines the mineral saturation indices. The saturation indices describe the saturation state of the dissolved species with respect to selected mineral phases. The saturation state is defined in terms of the saturation index (*SI*):

$$SI = \log \frac{IAP}{K}, \quad (10)$$

where *IAP* is the ion activity product and *K* is the equilibrium constant. The term *IAP/K* defines the ratio of the aqueous ion activity product to the solubility products in equilibrium with a given mineral phase. If the *SI* is less than zero, the ground water is undersaturated with respect to the mineral and the mineral will dissolve. If the *SI* is greater than zero, the water is saturated or supersaturated with respect to a mineral and the mineral may precipitate. Other factors, such as its stability in the presence of other minerals and kinetic factors, may also determine whether or not a mineral precipitates. Input data required for the speciation are a chemical analysis, field pH, temperature, alkalinity, and a specified Eh.

#### CARBON ISOTOPIC COMPOSITION

The carbon isotopic composition of the ground water is a critical constraint on the selection of mineral phases and identification of reactions, as the isotopic composi-

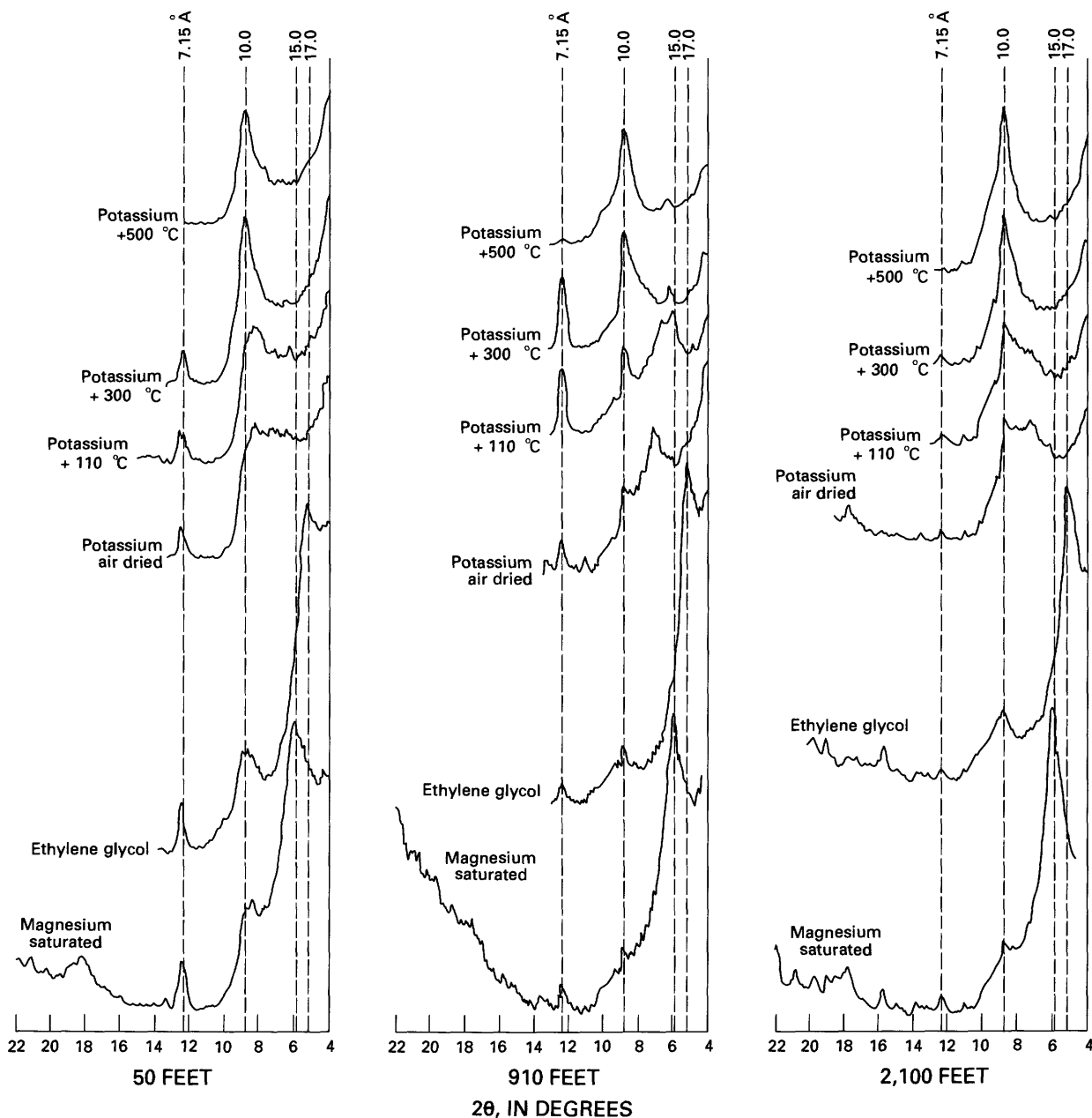


FIGURE 10.—X-ray diffraction patterns of less than 2-micrometer fractions of basin fill from well (D-9-1)13bbd in Vekol Valley. Depth of sample, in feet below land surface, given beneath figure.

tion is determined by reactions of gaseous(g) and aqueous(aq)  $\text{CO}_2$  with carbonate and silicate minerals. When minerals or gases are dissolved or precipitated, the isotopic composition of the water may change but should agree with the isotopic composition specified by the mass transfer and with known compositions of all carbon phases. The derived mass transfer in turn is determined by the selected phases and their stoichiometry. The isotopic composition of the carbon in solution determined from the general isotope mass-balance equation is

$$\sum_{p=1}^p \alpha_p b_{p,c} \delta^{13}\text{C}_p = \Delta m_T^{13}\text{C} \quad (11)$$

where

$$\Delta m_T^{13}\text{C} = (m_{T,c} \delta^{13}\text{C}_T)_{\text{final}} - (m_{T,c} \delta^{13}\text{C}_T)_{\text{initial}} \quad (12)$$

and the subscript  $T$  denotes total carbon.

The isotopic composition of the various carbon species is not fully defined for all geologic and hydrologic



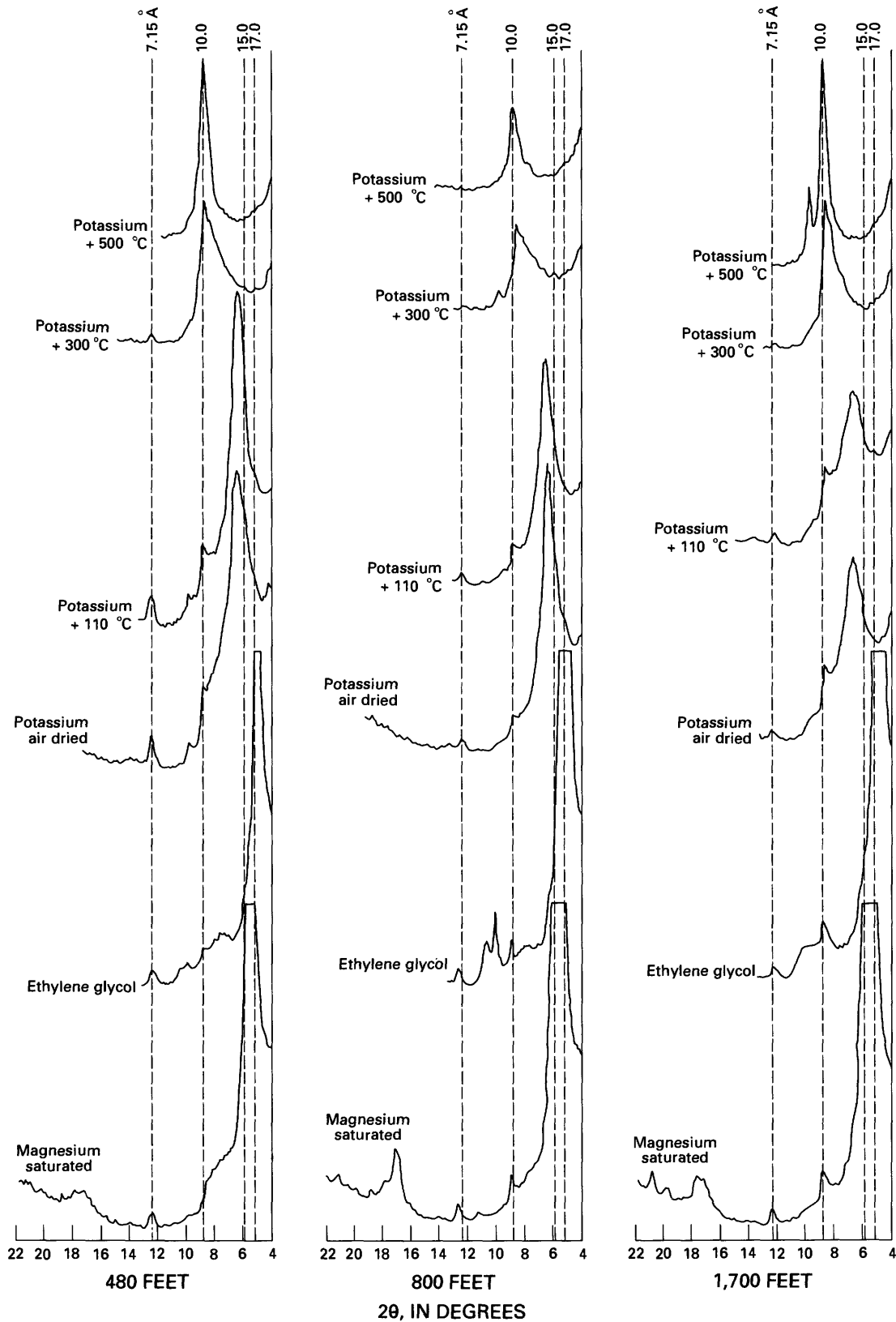


FIGURE 11.—X-ray diffraction patterns of less than 2-micrometer fractions of basin fill from well (C-5-3)29aaa in the Bosque basin, Gila Bend Plain. Depth of sample, in feet below land surface, given beneath figure.

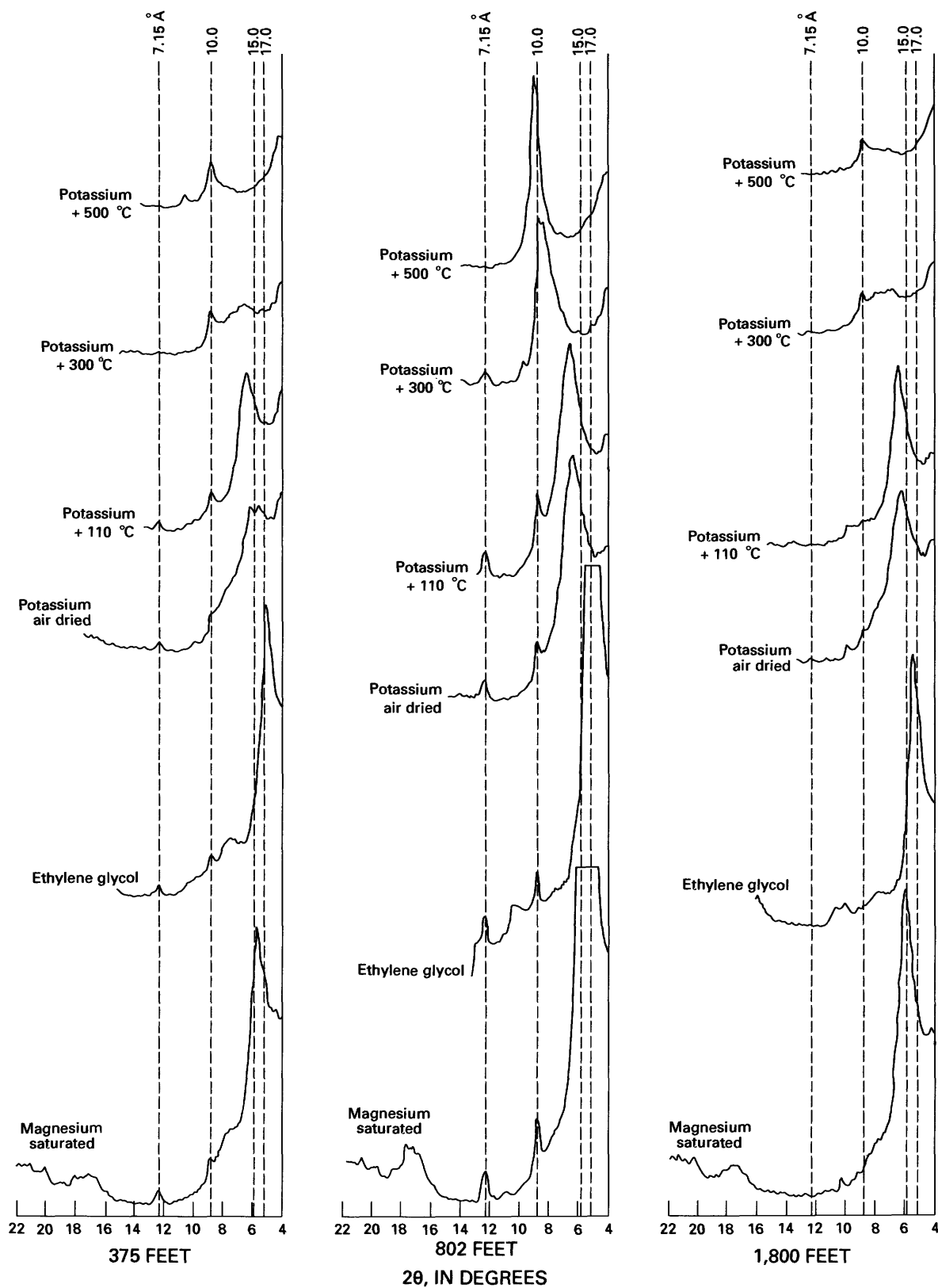


FIGURE 12.—X-ray diffraction patterns of less than 2-micrometer fractions of basin fill from well (D-2-8)26caa in East Salt River Valley. Depth of sample, in feet below land surface, given beneath figure.

environments, but published measurements for arid and semiarid areas allow reasonable estimates. In a study by Wallick (1973), the  $\delta^{13}\text{C}$  isotopic content of carbonates in soil and well core in the Tucson basin ranged from about  $-2$  to  $-6\text{‰}$  and averaged about  $-4\text{‰}$ . The  $\delta^{13}\text{C}$  content of the few carbonate samples determined during this study ranged from  $-1.8$  to  $-7.0\text{‰}$  and also averaged about  $-4.0\text{‰}$ . Published  $\delta^{13}\text{C}$  measurements of  $\text{CO}_2$  gas are fewer but indicate a soil-gas composition range of  $-15$  to  $-20\text{‰}$ . Wallick (1973, p. 122) determined a mean value of  $-15.12 \pm 2.88\text{‰}$  for five samples near Tucson, Ariz. Parada (1981) observed that  $\delta^{13}\text{C}$  of  $\text{CO}_2$  in desert soil near Tucson averaged  $-18\text{‰}$  and in river beds averaged  $-20\text{‰}$ .  $\text{P}_{\text{CO}_2}$  values reported in that study ranged from 0.001 to 0.05 atmospheres. Pearson and Hanshaw (1970) also reported values of  $-15$  to  $-19\text{‰}$  in the soil of arid west Texas.

### CHEMICAL EVOLUTION OF THE GROUND WATER

In determining the chemical evolution of the ground water in the individual basins, two distinct hydrochemical processes were identified: (1) reactions of meteoric water (pure water) as it infiltrates the soil zone and percolates through the unsaturated zone to the water table in the recharge area and (2) reactions of ground water as it moves from the recharge area downgradient to discharge areas.

A great deal of emphasis was placed on the evolution of the water in the recharge area, as many of the reactions are distinctly different from subsequent reactions along the flow paths. Major processes controlling recharge chemistry are the weathering of silicates and the dissolution of carbonate minerals in an acid environment. Both reactions consume protons. Reactions downgradient occur in an alkaline environment and although weathering of primary silicates continues, the relative amounts of primary silicates change and precipitation of calcium carbonate and probably of silica become dominant processes. In the recharge area, reactions of meteoric water, gases, and minerals may occur to a large degree in the soil and unsaturated zones. Downgradient, reactions occur only within the saturated zone.

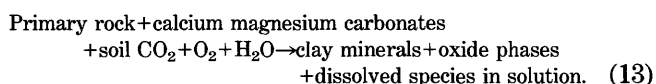
The compositions of recharge and downgradient waters used in the modeling do not balance perfectly in charge. Electrical neutrality was not attempted by adjusting any of the elements in solution. In development of the recharge and subsequent flow models, any imbalance was carried through the calculations, which in essence is distributing the imbalance equally among the dissolved species (Plummer, 1984).

### EVOLUTION OF THE GROUND WATER IN RECHARGE AREAS

The composition of the ground water in recharge areas is defined by an average of chemical analyses of water from wells in seven basins (table 2). Well selection was based on proximity to the mountains. Unfortunately, few wells were available for sampling in these areas, as most development occurs in the central parts of basins, where the land surface is flatter and the soil is better for agriculture. A greater number of wells in recharge areas is desirable because of the differences in the evolution of these waters and waters downgradient. The problem of poor well control may be minimized somewhat by the general uniformity of the water chemistry in recharge areas (as indicated by the relatively small standard deviations, especially of calcium, silica, and bicarbonate, the major constituents) relative to the variability of all ground water sampled. The large variability of all water sampled is reflected in the large standard deviations, which indicate that extreme values are influencing the mean values.

Feth and others (1964) showed that the chemistry of shallow and deep circulating springs could be related to the mineralogy and weathering of surrounding source rocks and to the equilibrium with secondary minerals. Garrels (1967) also used solute ratios to predict the compositions of the igneous rocks. However, the observed ground-water chemistry of the recharge area does not seem to reflect in all respects the primary rock composition. Magnesium concentrations in the ground water are variable and are distinctly greater than those expected from the weathering of primary rocks of the area, assuming that primary silicates are the source of magnesium. However, large silica concentrations suggest that hydrolysis of primary silicates is a major process, and, in a slowly fluxing system, the formation of secondary clay minerals would be expected. Sulfate and chloride concentrations, although generally small, become so significant that they require gypsum and halite as reactants.

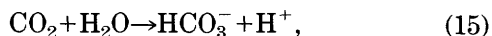
Reactions occurring in the recharge areas that can account for the observed water compositions are the weathering of primary silicates, chiefly feldspar and ferromagnesian minerals, and the dissolution of a calcium magnesium carbonate phase. The carbonate phase is selected to account for the large observed magnesium concentrations. These reactions, as well as subsequent reactions downgradient, can be described by a 13-component system— $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{SiO}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HF}$ ,  $\text{H}_2\text{O}$ —and can be written in the general form



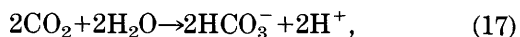
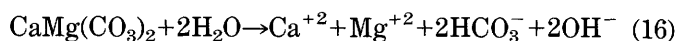
Assuming that the observed concentrations in the recharge area do indeed represent reactions of meteoric water with the source rock, two models that are compatible with the water composition were developed: (1) a mafic model for basalt-andesite rocks and (2) a felsic model for granite rocks. The models represent the two major rock associations of the mountains within the study area, as indicated by the bimodal distribution of plagioclase (fig. 9), the most obvious silicate source of calcium and sodium.

According to equation 13, the chemical evolution of ground water in recharge areas of basins having mafic terranes can be written to the following balanced hydrolysis and dissolution reactions:

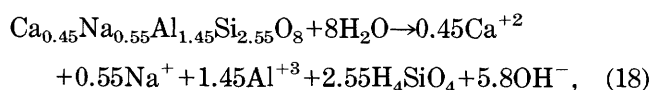
Hydrolysis of calcite:



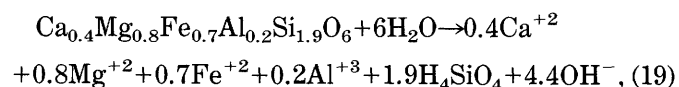
Hydrolysis of dolomite:



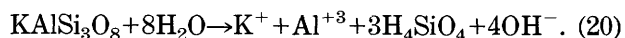
Hydrolysis of andesine:



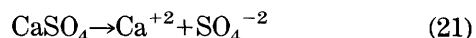
Hydrolysis of augite:



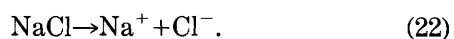
Hydrolysis of potassium feldspar (which for modeling purposes is specified as the sole source of potassium):



Other reactions occurring are the dissolution of gypsum (or anhydrite) and halite, respectively,

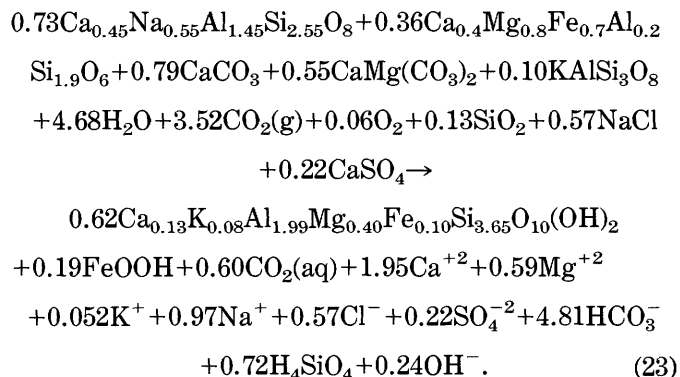


and

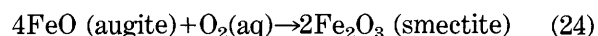


In determining the mass transfer of the silicate phases, it is assumed through the selection of the plausible phases that aluminum is conserved (that is, in eq. 8,  $\Delta m_{T,k}=0$ ) among the primary and secondary silicate phases and that montmorillonite is the controlling phase for magnesium and aluminum. Assuming conservation

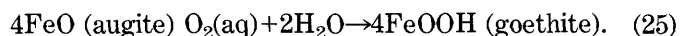
of mass, a summary equation for the recharge area can be written to the predominant dissolved species using values of  $\alpha_p$  for each phase and balanced dissolution reaction under observed pH and redox conditions:



Just as conservation of aluminum leads to no dissolved aluminum species appearing in the final summary equation, the oxidation of iron and its conservation in the solid phase also leads to no dissolved  $\text{Fe}^{+2}$  or  $\text{Fe}^{+3}$  appearing in the summary equation. The only aqueous species involving redox that explicitly appears in the equation is dissolved oxygen. Note that the iron-oxygen component of the redox reactions could be written in terms of oxide components, for example,



or



Analogously, similar reactions and mass transfer can be derived for the evolution of recharge waters in a felsic terrane using the corresponding mineralogy. The reactant and product phases used in the mafic and felsic models and the mass transfer derived by the models are listed in tables 3 and 4, respectively. Biotite and hornblende were used in the felsic model because they are common ferromagnesian minerals in granites in the study area. Table 4 shows that, in the evolution of the felsic water, smaller amounts of plagioclase and ferromagnesian minerals are weathered and slightly greater amounts of carbonate minerals are dissolved. This difference in weathering would be in agreement with weathering rates of the respective silicate minerals; sodic plagioclase and biotite show greater stability in the weathering environment than do the more calcic plagioclase and augite.

The chemical compositions of the reactant silicate minerals are consistent with the compositions of their respective rock types. The mass transfer associated with the primary minerals is expressed in oxide compositions

TABLE 3.—Phases used for derivation of mass transfer

Reactant phases	Stoichiometry
Calcite.....	$\text{CaCO}_3$
Dolomite.....	$\text{CaMg}(\text{CO}_3)_2$
Oligoclase.....	$\text{Ca}_{0.25}\text{Na}_{0.75}\text{Al}_{1.25}\text{Si}_{2.75}\text{O}_8$
	$\text{Ca}_{0.30}\text{Na}_{0.70}\text{Al}_{1.30}\text{Si}_{2.70}\text{O}_8$
Andesine.....	$\text{Ca}_{0.33}\text{Na}_{0.67}\text{Al}_{1.33}\text{Si}_{2.67}\text{O}_8$
	$\text{Ca}_{0.45}\text{Na}_{0.55}\text{Al}_{1.45}\text{Si}_{2.55}\text{O}_8$
Potassium feldspar.....	$\text{KAlSi}_3\text{O}_8$
Augite.....	$\text{Ca}_{0.4}\text{Mg}_{0.8}\text{Fe}_{0.7}\text{Al}_{0.2}\text{Si}_{1.9}\text{O}_6$
Hornblende.....	$\text{CaMgFeAlSi}_{3.5}\text{O}_{11}\text{OH}$
Biotite.....	$\text{KMg}_{1.5}\text{Fe}_{1.5}\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
Silica (volcanic glass, quartz).	$\text{SiO}_2$
Halite.....	$\text{NaCl}$
Gypsum (anhydrite).....	$\text{CaSO}_4$
Fluorite.....	$\text{CaF}_2$
Aqueous phase.....	$\text{H}_2\text{O}, \text{CO}_2, \text{O}_2$
Product phases	Stoichiometry
Calcite.....	$\text{CaCO}_3$
Montmorillonite (mafic).....	$\text{Ca}_{0.13}\text{K}_{0.07}\text{Mg}_{0.40}\text{Fe}_{0.10}\text{Al}_{1.99}$
	$\text{Si}_{3.65}\text{O}_{10}(\text{OH})_2$
Montmorillonite (felsic).....	$\text{Ca}_{0.10}\text{K}_{0.13}\text{Mg}_{0.40}\text{Fe}_{0.10}\text{Al}_{1.99}$
	$\text{Si}_{3.65}\text{O}_{10}(\text{OH})_2$
Kaolinite.....	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_8$
Goethite.....	$\text{FeOOH}$
Silica (chalcedony).....	$\text{SiO}_2$
Aqueous phase.....	$\text{Ca}^{+2}, \text{Mg}^{+2}, \text{Na}^+, \text{K}^+, \text{Al}^{+3},$ $\text{Fe}^{+3}, \text{Cl}^-, \text{SO}_4^{-2}, \text{F}^-,$ $\text{HCO}_3^-, \text{H}_4\text{SiO}_4$

in table 5. Chemical analyses of the bulk-rock fraction of the basin fill from Vekol Valley and the Bosque basin in Gila Bend Plain are shown in table 6. The chemical composition of the derived phases in table 5 are in general agreement with the composition of the basin fill from Vekol Valley, a basin bounded by basaltic and andesitic rocks, and from the Bosque basin, a basin surrounded by granitic intrusive rocks. Published average compositions for three rock types also are given in table 6. The minerals and the rock types derived from the modeling indicate reactions of water with an andesite and with a granodiorite or a monzonite. The computed oxide compositions for the felsic model shown in table 6 are normalized to 20 percent additional quartz because granites contain 25 percent free quartz and granodiorites and quartz diorites contain about 20 percent free quartz (Barth, 1967, p. 56). The normalized compositions agree better with published data, as the quartz component of the rock is not represented in the water composition owing to its low solubility.

The chemical compositions of the model-derived mineral phases indicate that aluminum is about 3 to 5 percent higher and that potassium is slightly lower than in the field-measured and reported rock types. The recharge water does not appear to contain the potassium concentrations that would be expected from the weathering of

TABLE 4.—Summary of mass transfer for recharge waters  
[Values\* in millimoles per kilogram  $\text{H}_2\text{O}$ . Dashes indicate phase not used]

Phases	Basalt-andesite	Granite	
		Hornblende	Biotite
$\text{O}_2$ .....	0.06	0.05	0.05
$\text{CO}_2$ .....	3.52	3.36	3.19
Calcite**.....	.79	.86	1.06
Dolomite**.....	.55	.59	.58
Andesine( $\text{An}_{45}$ ).....	.73	—	—
Oligoclase( $\text{An}_{25}$ ).....	—	.54	.54
Potassium feldspar.....	.10	.12	.11
Augite.....	.36	—	—
Hornblende.....	—	.19	—
Biotite.....	—	—	.13
Silica.....	.13	.01	.19
Halite.....	.57	.57	.57
Gypsum.....	.22	.22	.22
Montmorillonite (mafic).....	-.62	—	—
Montmorillonite (felsic).....	—	-.49	-.46
Goethite.....	-.19	-.14	-.15

\*Reactants are positive and products are negative.

\*\*Computed as a single calcium magnesium phase.

most primary rocks. The smaller potassium concentrations may be explained by little breakdown of the potassium feldspars relative to the plagioclase feldspars as suggested by Garrels and MacKenzie (1967) for the genesis of spring waters. More likely, however, from evidence presented later, the smaller concentrations probably reflect adsorption of solute potassium by smectite clays rather than differential weathering. Reasons for the apparently higher aluminum content are discussed later.

The maximum, minimum, and average saturation indices of the ground water with respect to a number of minerals observed or postulated within the aquifer or unsaturated zone are given in table 7. The ground water is undersaturated with respect to albite and anorthite, which are the end members of the plagioclase series, and

TABLE 5.—Major oxides calculated from derived mineral phases  
[In weight percent]

	Basalt-andesite	Granite	
		Hornblende	Biotite
CaO.....	8.42	7.04	*5.63
Na <sub>2</sub> O.....	3.95	4.85	3.88
MgO.....	3.69	2.96	2.36
FeO**.....	5.74	5.28	4.22
Al <sub>2</sub> O <sub>3</sub> .....	19.92	19.40	15.52
SiO <sub>2</sub> .....	56.77	58.29	66.64
K <sub>2</sub> O.....	1.50	2.18	1.75
		4.63	3.71

\*Normalized to additional 20 percent quartz.

\*\*All iron reported as FeO.

TABLE 6.—*Chemical analyses of basin fill from Vekol Valley and the Bosque basin and average compositions of selected rock types*

[In weight percent. Analyses by Center for Meteorite Studies, Arizona State University]

	Vekol Valley* (D-9-1)13bbd	Bosque Basin** (C-6-3)2acd	Effusive andesite†	Plutonic granodiorite‡	Plutonic monzonite‡
CaO .....	6.84	3.38	8.13	3.61	6.92
Na <sub>2</sub> O .....	2.62	2.76	3.77	3.90	3.59
MgO .....	3.97	1.82	4.47	1.59	3.76
Fe <sub>2</sub> O <sub>3</sub> †† .....	4.95	5.70	9.21	3.98	7.32
Al <sub>2</sub> O <sub>3</sub> .....	14.27	13.85	17.63	15.90	16.97
SiO <sub>2</sub> .....	63.80	68.66	55.65	67.90	56.65
K <sub>2</sub> O .....	3.55	3.83	1.14	3.12	4.79

\*Average values of four stratigraphic intervals.

\*\*Average values of seven stratigraphic intervals.

†From Barth, 1967, p. 58.

††All iron reported as Fe<sub>2</sub>O<sub>3</sub>.

with potassium feldspar (adularia). Plagioclase and probably potassium feldspar occur in the basin fill only as primary minerals. The ground water is highly undersaturated with respect to the ferromagnesian minerals diopside and clinoenstatite (pyroxenes), tremolite (amphibole), and forsterite and the minerals gypsum and halite. As expected, these minerals generally are not observed in the basin fill. The water is supersaturated with respect to the clay minerals montmorillonite, kao-

linite, and K-mica (muscovite), the zeolites laumontite and leonhardite, and the aluminum and iron oxide minerals boehmite and goethite. The solution is at equilibrium with respect to calcite and dolomite. Zeolites are rarely present in the basin fill; clinoptilolite was detected in two samples. Muscovite, a low-temperature primary mineral common to igneous and metamorphic rocks, is ubiquitous in the clay and bulk-rock fraction and appears to weather very little or not at all. The most stable phase is montmorillonite, as suggested by its abundance in the basin fill as well as its saturation state.

TABLE 7.—*Maximum, minimum, and average saturation indices of the recharge waters with respect to various mineral phases*

[Phases and thermodynamic data from Ball and others (1980)]

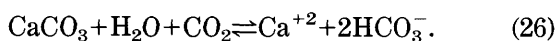
Phases	Number of samples	Maximum	Minimum	Average
Adularia.....	5	0.033	-0.418	-0.187
Albite.....	5	-1.247	-1.816	-1.544
Al(OH) <sub>3</sub> .....	5	-1.097	-1.382	-1.251
Anorthite.....	5	-2.604	-3.094	-2.850
Beidellite.....	5	3.299	2.174	2.866
Boehmite.....	5	.721	.433	.562
Calcite.....	7	.455	-.067	.129
Chalcedony.....	7	.434	.190	.326
Clinoenstatite.....	7	-2.495	-3.908	-3.413
Diopside.....	7	-2.008	-4.469	-3.543
Dolomite.....	7	.769	-.724	-.225
Fluorite.....	7	-1.460	-2.619	-2.025
Forsterite.....	7	-7.523	-10.210	-9.256
Goethite.....	7	5.494	5.112	5.324
Gypsum.....	7	-1.516	-3.786	-2.408
Halite.....	7	-7.691	-8.688	-8.001
Kaolinite.....	5	3.055	2.194	2.681
K-mica.....	5	1.005	.204	.544
Laumontite.....	5	2.012	1.304	1.805
Leonhardite.....	5	11.755	10.339	11.367
Montmorillonite CA.....	5	3.175	2.054	2.726
Montmorillonite BF.....	5	4.859	4.267	4.615
Montmorillonite AB.....	5	3.768	3.294	3.638
Phillipsite.....	5	.087	-.316	-.073
Sepiolite <sub>(c)</sub> .....	7	-1.316	-4.337	-3.310
Tremolite.....	7	2.649	-6.885	-3.400

In considering the thermodynamics of the saturation state of the ground water with respect to the clay minerals, a problem arises with the dissolved-aluminum data. To define the saturation state accurately, the concentrations in solution of all elements present in the minerals must be known. In examining aluminum concentrations in stream waters, Jones and others (1974) determined that dissolved-aluminum concentrations would have to be less than 0.5 µg/L for the waters to be in equilibrium with kaolinite or montmorillonite. The average concentration of dissolved aluminum determined for the study area was considerably higher, about 10 µg/L. These aluminum concentrations may be the result of colloidal or particulate clay that passes through the 0.1-µm pore-size filter and may not represent dissolved molecular aluminum. Acidification of samples by standard procedures prior to analysis would transfer all the particulates to the aqueous phase. The supersaturation of the clay minerals may be caused by the large aluminum concentrations as well as a supersaturated solution.

Inclusive in the derivation of the primary mineral phases and the mass balance of magnesium are considerations of the isotopic composition of the solution. The reactions and mass transfer shown in equation 23 and in table 4 satisfy both stoichiometric and isotopic requirements. In determining the reactions in the recharge area, it is assumed that the dissolution of the carbonate

minerals is congruent and that isotopic equilibrium does not occur between the  $\text{CO}_2(\text{g})$  in the soil zone and the bicarbonate in solution at depth. The isotopic composition of the total inorganic carbon in solution is estimated to be  $-12.5\text{‰}$  on the basis of  $\delta^{13}\text{C}$  values of samples taken near recharge areas. Using the isotope mass-balance equation (eq. 11) and molality values determined by the mass transfer and a  $\delta^{13}\text{C}$  value of  $-4.0\text{‰}$  for the solid carbon species, a  $\delta^{13}\text{C}$  value of  $-17\text{‰}$  for the  $\text{CO}_2$  gas [ $\delta^{13}\text{CO}_2(\text{g}) \sim \delta^{13}\text{CO}_2(\text{aq})$ ] was determined for the mafic model and a  $\delta^{13}\text{C}$  value of  $-18\text{‰}$  for the felsic model. A predicted  $\delta^{13}\text{C}$  value of  $-17$  to  $-18\text{‰}$  for the  $\text{CO}_2$  gas is in agreement with reported values. The general agreement between the selected mineral phases, the derived  $\delta^{13}\text{C}$  isotopic composition of the solution, and the measured or reported  $\delta^{13}\text{C}$  values suggest that the reactions are indeed congruent and that the reactions of carbon during recharge involve little fractionation.

The reactions that describe the carbon chemistry during recharge apply to mountain-front recharge and may not apply to recharge along streams. In the alluvial aquifers of basins along the Colorado River, for example, where water levels are shallow, approximately 10 ft below land surface, the aquifer may be open to soil  $\text{CO}_2$ . The higher and more variable bicarbonate values observed in these shallow systems would be consistent with a large reservoir of  $\text{CO}_2$  in the soil zone. The bicarbonate concentrations thus would be a function of a constant  $P_{\text{CO}_2}$  and the availability of calcite for dissolution:



Under these open conditions, the soil  $\text{CO}_2(\text{g})$  may be in isotopic equilibrium with the dissolved bicarbonate in the aquifer and lead to an enrichment of  $\delta^{13}\text{C}$  of the bicarbonate in solution to a similar value of about  $-12\text{‰}$  (Deines and others, 1974).

The derived chemical and isotope mass balance for the recharge waters is based on an assumed  $\delta^{13}\text{C}$  value of  $-4\text{‰}$  for the solid carbonate phase and implies that the isotopic composition of dolomite is the same as that of calcite. Although the carbon mass transfer would not be affected by the choice of either calcite or dolomite as reactants, the derived mass transfer of the other phases is altered substantially if the isotope content of dolomite or calcite differs significantly from  $-4.0\text{‰}$ . Most of the available carbonate isotope analyses are of caliche, a layered, sparingly soluble calcium carbonate deposit commonly found in desert soils. Until more is known about the  $\delta^{13}\text{C}$  of the carbonates as well as all carbon phases, little more can be said regarding the carbonate evolution of the ground water. Because phases other than dolomite could be considered sources of magnesium (for example, palygorskite was strongly indicated in the

unsaturated zone in Vekol Valley), evidence for the selection of dolomite will be presented.

The XRD analyses of the basin fill provide conclusive evidence that dolomite as well as calcite is an abundant mineral. Dolomite was confirmed at varying depths in the fine-sand (200- $\mu\text{m}$ ) fraction of the unsaturated zone but was not confirmed in the saturated zone (table 8). XRD analyses of soil samples show only calcite present in the upper few inches but dolomite present in small to moderate amounts at 60 in (fig. 13). Dolomite was detected at depths between 70 and 215 ft below land surface in the unsaturated zone of West Salt River Valley near the White Tank Mountains and, surprisingly, was detected at a depth of 101 ft near the center of the basin at about a 10:1 ratio over calcite. The XRD patterns of the basin fill are shown in figure 13. The analyses indicate that dolomite may be ubiquitous in the unsaturated zone; dolomite appears to be partially leached in the unsaturated zone but totally leached in the saturated zone.

Dolomite has been reported by other researchers in similar geologic environments. Barnes and O'Neil (1971) found magnesian calcites and dolomites in Holocene conglomerate cements and travertines of the Coast Range, with solid solutions ranging from  $\text{Ca}_{0.51}\text{Mg}_{0.49}$  to  $\text{CaCO}_3$  for calcite and  $\text{Ca}_{0.58}\text{Mg}_{0.42}\text{CO}_3$  to  $\text{Ca}_{0.51}\text{Mg}_{0.49}\text{CO}_3$  for dolomites. On the basis of  $^{18}\text{O}$  and  $\text{MgCO}_3$  content, they believed that the carbonates were direct precipitates and not magnesium substitutions of calcite. They also observed that such mechanisms as capillary pumping as well as complete evaporation may result in a constant chemical environment suitable for the formation of calcium magnesium carbonates.

TABLE 8.—*Distribution of calcite and dolomite in the unsaturated zone*

[X-ray diffraction analyses by David M. Hendricks, University of Arizona]

Well location	Depth below land surface	Amount of calcite	Amount of dolomite
(D-19-1)8ddd . . . . . Great Plain near San Simon Wash basin	170 feet	Moderate	Trace
(A-6-5)31bcc. . . . . Paradise Valley adjacent to McDowell Mountains	20 feet	Moderate	Moderate
(C-15-2)19bab. . . . . San Simon Wash area	110 feet 190 feet	Moderate Moderate	Small Small
(B-2-1)5abc2. . . . . Center of West Salt River Valley	101 feet	Small	Large
(B-2-2)34bcb. . . . . West Salt River Valley near White Tank Mountains	70 feet 50 feet 175 feet 215 feet	Large Moderate Moderate Small	Large Large Moderate Trace
(D-16-25)4cdd. . . . . Willcox basin near playa	10 inches 60 inches	Moderate Large	None Moderate

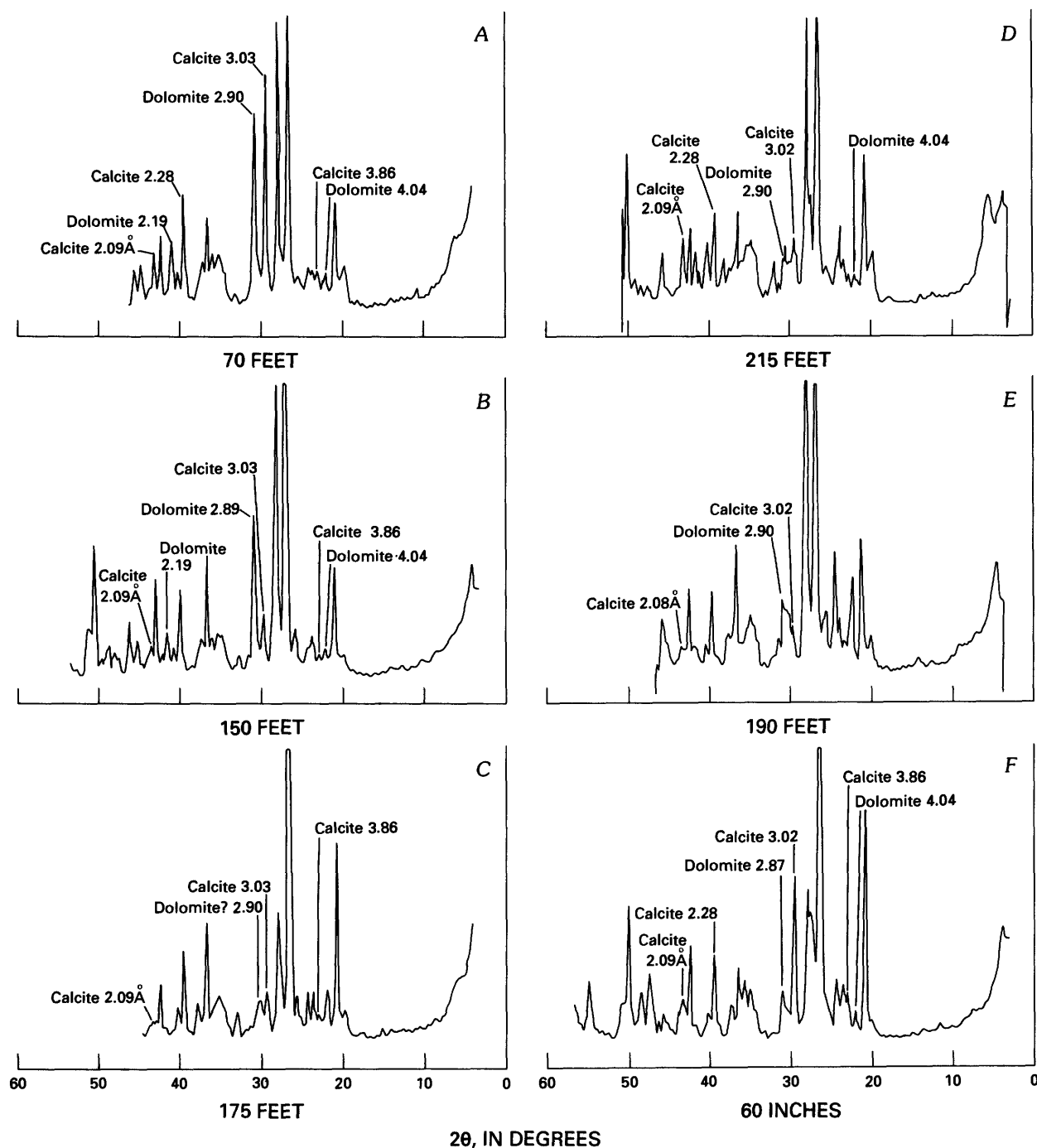


FIGURE 13.—X-ray diffraction patterns of 200-micrometer fractions of basin fill from the unsaturated zone. Samples A–D are from well (B-2-2)34bcb, sample E is from well (C-15-2)19bab, and sample F is a soil sample from well (D-16-25)4cdd. Depth of sample, in feet or inches below land surface, given beneath figure.

Analyses of springs also provide indirect evidence of the existence of a magnesium carbonate phase. Springs that emerge near recharge areas commonly have compositions similar to recharge waters. Concentrations of major ions in spring water fall well within the standard deviation for the recharge waters, with the exception of

silica, whose concentration in spring water is only about 30 percent as large as in the recharge waters. The small silica concentrations indicate that the weathering of silicates is less important, even though similar reactions may be occurring in recharge and spring waters, accounting for the calcium, magnesium, and bicarbonate



concentrations. Spring discharge waters are often controlled by fault or fracture systems, which may provide a direct route from recharge to discharge, diminishing residence and reaction times. The walls of fracture systems may become coated with precipitates, which also can inhibit the reactions of the silicates.

#### MOVEMENT OF WATER AND REACTIONS IN THE UNSATURATED ZONE

The compositions of runoff and precipitation entering the soil and unsaturated zones in recharge areas are unknown, but the compositions of streams that reflect surface runoff provide some information. Analyses of four streams sampled near their sources are shown in table 9. The samples taken during high discharge represent runoff, and those taken during low discharge probably include a large base-flow component. Important observations are that calcium and magnesium are the major cations, that the calcium to magnesium molar ratios range from about 60:40 to 67:33, and that calcium and magnesium are in solution as carbonates, as indicated by the small sulfate and chloride concentrations. Calcium and magnesium carbonates seem readily available in runoff waters. The high magnesium to calcium ratio of the water relative to the magnesium to calcium ratio of the source rocks may be due to greater alteration of the less stable ferromagnesian minerals relative to plagioclase. A slight alteration of ferromagnesian minerals could account for the observed compositions when considering the large volumes of exposed rocks within the drainage areas. Miller and Drever (1977) found similar calcium to magnesium ratios in streams draining the Absoroka Mountains in Wyoming, which they attributed to slight alteration of large volumes of rocks.

The streams listed in table 9 drain large areas and thus may contain larger solute concentration than does runoff that recharges the basin aquifers. The runoff presumably

would drain smaller areas and would not experience deep percolation or long residence times. The runoff shown in table 9 contains an average bicarbonate concentration of about 1 mmol/L, which suggests that most of the bicarbonate concentrations are acquired through dissolution of carbonates after infiltration.

The mechanism by which  $\text{CO}_2(\text{g})$  enters and is transported through the unsaturated zone has not been defined.  $\text{CO}_2$  is undoubtedly transported in the aqueous phase through the unsaturated zone via deep percolation, but other mechanisms seem possible. Thorstenson and others (1983), in work in the western Great Plains, determined that diffusion of gaseous species of  $\text{CO}_2$  is an important transport mechanism in the unsaturated zone. Movement by diffusion of  $\text{CO}_2$  of more than 50 ft to the water table was observed. Because little is known about movement of gas or liquid in arid climates where depths to water are on the order of 600 to 800 ft,  $\text{CO}_2$  movement is assumed for modeling purposes to occur in the aqueous phase via deep percolation during recharge by a series of pulses or slugs, probably along permeable preferential vertical flow paths. At some point during recharge, the system may become closed to  $\text{CO}_2$  and other gases; the exceptionally great depths to water may preclude direct interaction of soil  $\text{CO}_2$  with carbonate minerals in the aquifer.

At equilibrium, the high partial pressure of  $\text{CO}_2$  in the soil zone provides dissolved  $\text{CO}_2$  (carbonic acid) for the weathering process. The average  $\text{CO}_2$  pressure of the recharge water is about  $10^{-1.7}$ , which is considerably higher than atmospheric ( $\sim 10^{-3.5}$ ). The relation between  $P_{\text{CO}_2}$  and dissolved  $\text{CO}_2$  is shown by the equation



and because  $\text{H}_2\text{CO}_3(\text{aq})$  is an acid, it disassociates and forms hydrogen and bicarbonate ions:



TABLE 9.—Chemical analyses of selected streams in Arizona

[In millimoles per liter except as indicated; ft<sup>3</sup>/s, cubic feet per second; °C, degrees Celsius; mg/L, milligrams per liter. Dashes indicate no data. Data from U.S. Geological Survey, 1980]

Station name	Date sampled	Discharge (ft <sup>3</sup> /s)	pH	Temperature (°C)	Dissolved oxygen (mg/L)	Calcium (Ca <sup>+2</sup> )	Magnesium (Mg <sup>+2</sup> )	Sodium (Na <sup>+</sup> )	Potassium (K <sup>+</sup> )	Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	Sulfate (SO <sub>4</sub> <sup>-2</sup> )	Chloride (Cl <sup>-</sup> )	Fluoride (F <sup>-</sup> )	Silica (SiO <sub>2</sub> )
Verde River near . . . . .	3-13-79	1,130	7.6	10.0	9.7	0.37	0.23	0.22	0.03	1.13	0.05	0.021	0.01	0.23
Clarksdale	11-14-79	149	7.5	9.0	11.6	.75	.38	.43	.07	2.13	.09	.42	.01	.23
	5-9-78	80	8.3	17.0	10.4	1.40	.95	1.00	.06	4.91	.13	.28	.01	.25
Oak Creek near . . . . .	1-17-79	*2,500	—	4.5	11.7	.22	.19	.08	.02	.80	.05	.03	.00	.16
Sedona	5-10-79	43	8.5	11.0	9.3	1.15	.66	.20	.03	2.79	.05	.03	.01	.22
	3-14-79	*500	8.1	5.5	11.2	.27	.19	.09	.01	.80	.06	.04	.00	.20
Burro Creek above . . . .	4-4-79	76	—	15.5	8.7	.65	.45	1.04	.11	2.86	.15	.18	.01	.60
Boulder Creek	6-12-79	5.0	8.2	20.5	7.6	.77	.74	2.47	.19	—	.32	.76	.03	.47
near Bagdad	7-12-79	1.9	8.3	28.0	8.3	.60	.70	2.95	.22	—	.45	1.02	.04	.56
Burro Creek at . . . . .	1-17-79	14,400	—	7.0	12.0	.30	.15	.24	.05	1.01	.06	.05	.01	.04
U.S. 93 near	5-9-79	11	7.6	18.0	7.9	1.50	1.48	2.04	.18	—	1.24	.87	.05	.47
Bagdad	11-15-78	225	8.7	11.0	11.5	.57	.40	.78	.09	1.56	.35	.48	.03	.60

\*Estimated.

The hydrogen ion, which provides the impetus for the weathering process, dissolves carbonate minerals and attacks the lattice structure of the silicates, releasing cations and silica. The aggressiveness of dissolved  $\text{CO}_2$  is indicated by the noticeable absence of caliche in some of the arroyos and washes near the mountains.

#### EVOLUTION OF THE GROUND WATER IN SELECTED BASINS

Chemical models were developed along general flow paths for selected basins using compositions observed in the recharge areas as initial water compositions and compositions observed downgradient as final water compositions. The final water composition is that of the farthest downgradient point, normally the center or downvalley part of the basin. Reactant mineral phases used in the models were chosen to be consistent with the basin geology. Compositions of reactant and product phases were idealized and were used consistently within and among basins to confirm the presence or absence of similar reactions. Reactions also were used consistently among basins, although a particular reaction, for example, ion exchange, may not pertain to all basins. The chemical models are described by basin, rather than by individual reaction simultaneously for all basins, to provide a clear picture of evolution in each basin.

The basins were selected to illustrate climatic and physiographic differences or distinctive geohydrologic and geochemical characteristics (fig. 14). Vekol Valley (southern part) was selected as typical of the medium-sized oval basins in arid south-central Arizona where sufficient well data and test holes were available for analysis. Lower San Pedro Valley was selected as an excellent example of the long, narrow basins in the southeast where the alluvial aquifer is confined and flowing wells exist and where distinct flow paths can be delineated. Ranegras Plain in the western arid region has a markedly different geochemistry exemplified by large concentrations of dissolved solids and occurrences of trace elements in the ground water. McMullen Valley is one of the few basins in the study area bounded by intrusive felsic rocks. The Willcox basin is typical of the large oval basins in southeastern Arizona where precipitation and ground-water recharge are relatively high and much of the annual recharge may occur along the valley floor. A generic model for basins along the Colorado River (Yuma area in fig. 14) is presented as an alternative to previously published explanations for the genesis of the ground water underlying the flood plain.

Some basins for which a large amount of well and chemical data have been collected, such as basins in the Phoenix, Tucson, and Yuma areas, were not selected for modeling. These basins have complex hydrologic sys-

tems and have been extensively developed, which substantially altered the hydrologic and chemical systems, thus making the modeling interpretations difficult or impossible.

The recharge areas of the basins were defined as those areas in basins adjacent to mountains receiving the highest annual precipitation. Hydrologic information from previously published studies was also considered. Analytical data for selected wells in the modeled basins are summarized in table 10.

The chemical models are divided into two fundamental types—closed systems and open systems. Closed systems are those that do not receive additional recharge along the flow path after the initial recharge or are not influenced by liquid or gas phases other than those introduced during initial recharge. In closed systems the aqueous chemistry is determined solely by the reactions of the initial recharge water with the various minerals as it moves downgradient. Conversely, open systems are those whose aquifer chemistry is in part controlled or influenced by atmospheric gases or liquids that enter the system along flow paths subsequent to initial recharge. In the development of basin models it will be shown that the chemistry of most of the basins evolves under closed conditions.

#### VEKOL VALLEY

The southern part of Vekol Valley is an oval basin about 14 mi long and 13 mi wide (measured at the mountain front) (fig. 15); it is typical in shape and geology of many basins in arid south-central Arizona. The ground water contains low dissolved solids, about 400 mg/L, which also is typical of many basins in the area. The basin is bounded on the east by schist, granite, and andesite of the Table Top and Vekol Mountains and on the west by andesite, basalt, and schist of the Sand Tank Mountains (Wilson and others, 1969).

Lithologic and geophysical logs of several wells throughout the basin show that the alluvial aquifer consists of several hundred feet of sand and gravel overlain throughout much of the basin by a thick silt-clay unit. In ascending order, the basin fill in the central part of the basin consists of about 500 ft of silty sand, gravel, and conglomerate; 950 ft of sandy gravel; 500–550 ft of silt and clay; and 50–100 ft of sand and gravel. The depth to water in the central part is between 400 and 450 ft below land surface (Wilson, 1979). The major recharge area in the basin is adjacent to the Sand Tank Mountains, which are the dominant mountain range in the area and receive the highest precipitation. Ground-water flow is eastward toward the center of the basin and eventually southward out of the basin. A buried ridge to the north forms a ground-water divide between this south basin

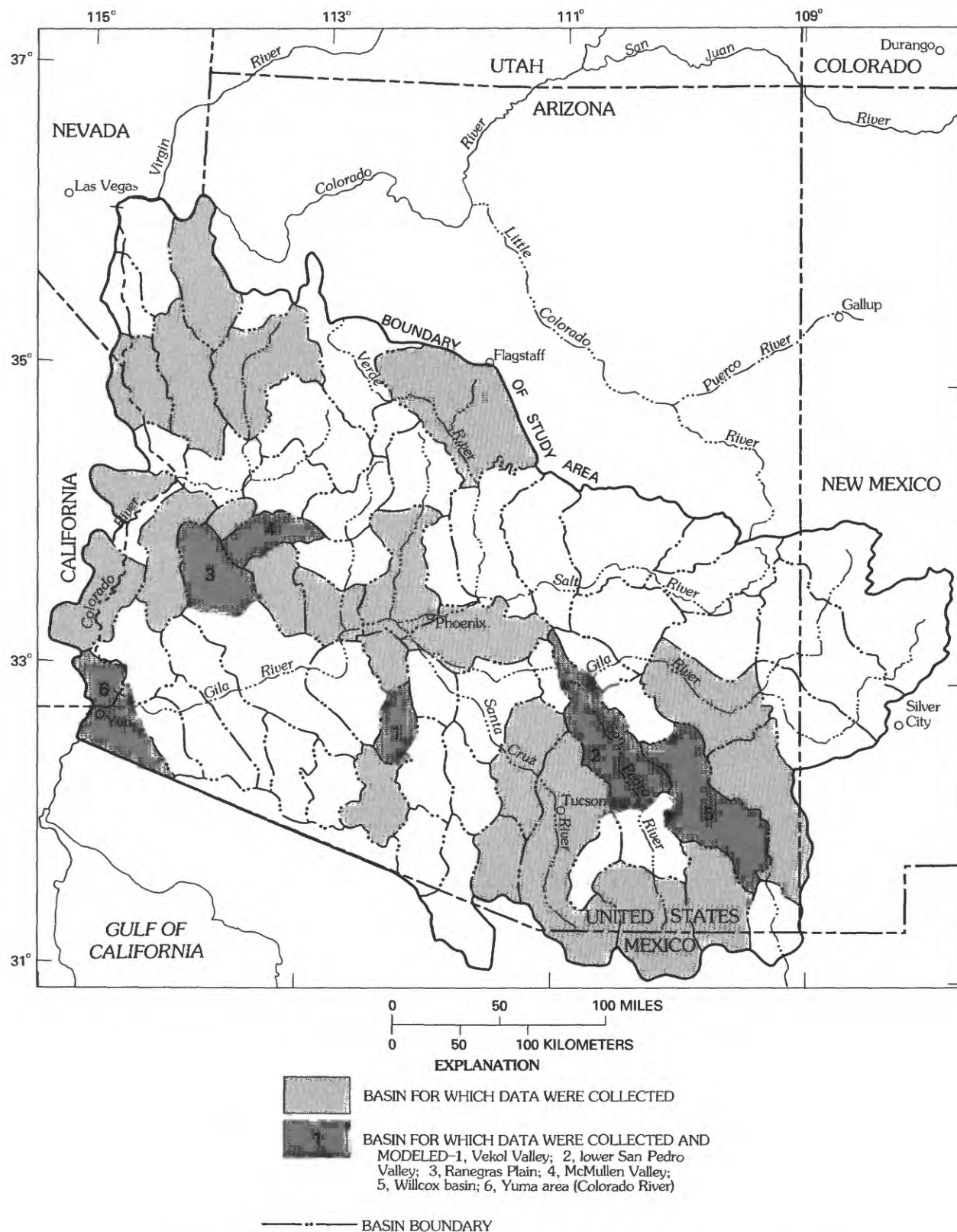


FIGURE 14.—Basins for which data were collected and for which models were developed.

TABLE 10.—Analytical data for selected wells in Vekol Valley, lower San Pedro Valley, Ranegras Plain, McMullen Valley, and the Willcox basin

[In millimoles per liter except as indicated; °C, degrees Celsius; meq/L, milliequivalents per liter; mg/L, milligrams per liter. Vek, Vekol Valley; LSP, lower San Pedro Valley; Ran, Ranegras Plain; McM, McMullen Valley; Wil, Willcox basin; well names keyed to figures. Dashes indicate no data]

Well location	Well name	Well depth, in feet	pH	Temperature (°C)	Field alkalinity (meq/L)	Ca <sup>+2</sup>	Mg <sup>+2</sup>	K <sup>+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	F <sup>-</sup>	SiO <sub>2</sub>	Log <sup>p</sup> CO <sub>2</sub> *	NO <sub>3</sub> <sup>-</sup> -N	Dissolved solids (mg/L)
(D-8-1)31cbd . . .	Vek 1	715	7.4	36.5	3.560	0.748	0.576	0.043	2.436	0.592	0.271	0.037	0.799	-1.98	0.286	324
(D-9-1)11dbd1 . . .	Vek 2	1,738	8.0	37.0	2.083	.325	.066	.079	5.220	1.918	.750	.032	.699	-2.80	.543	421
(D-9-1)13bbd . . .	Vek 3	1,975	8.0	36.5	1.917	.324	.091	.168	5.655	2.200	.988	.026	.732	-2.88	.593	524
(D-11-18)3cdc . . .	LSP 1	387	8.3	26.5	2.373	.232	.045	.046	2.784	.310	.198	.105	.583	-3.09	.114	223
(D-8-17)32daa . . .	LSP 2	1,485	8.4	42.0	1.822	.245	.002	.064	5.655	1.241	1.457	.417	.566	-3.26	.023	417
(B-4-15)14caa . . .	Ran 1	900	8.4	34.2	.359	6.736	.033	.069	13.050	3.667	11.451	.526	.266	-4.69	—	1,830
(B-4-15)18bbc . . .	Ran 2	870	8.1	27.0	1.442	.674	.128	.094	7.395	3.384	1.770	.279	.649	-3.20	.357	649
(B-4-15)18bbb . . .	Ran 3	1,005	7.7	29.0	.951	6.487	.202	.113	8.700	3.949	8.120	.190	.533	-2.97	.328	1,530
(B-8-17)32dda . . .	Ran 4	1,100	7.7	26.0	1.978	8.483	3.292	.306	41.304	22.568	19.779	.234	.433	-2.82	1.356	4,325
(B-6-13)25bbb . . .	McM 1	930	7.8	33.0	3.048	.574	.300	.082	3.828	1.185	.468	.074	.399	-2.50	.228	338
(B-5-13)1cba . . .	McM 2	730	8.2	31.0	2.491	.185	.074	.046	4.785	1.326	.541	.111	.349	-3.00	.257	343
(B-7-8)17bbc . . .	McM 3	1,896	7.9	30.0	2.398	.325	.247	.066	2.306	.395	.219	.253	.399	-2.68	.114	218
(B-8-9)32baa . . .	McM 4	1,003	9.4	33.5	1.645	.035	.000	.013	4.785	1.382	.469	.200	.399	-4.12	.221	156
(D-17-27)31ddd . .	Wil 1	555	8.0	22.0	2.065	.424	.074	.026	1.392	.150	.035	.126	.666	-2.92	.034	162
(D-17-26)25bad . .	Wil 2	1,020	8.4	22.0	1.999	.375	.066	.028	1.871	.223	.136	.232	.570	-3.48	.079	183
(D-16-26)9daa . .	Wil 3	460	8.0	24.5	2.032	.824	.095	.064	1.740	.279	.635	.116	.466	-2.43	.001	239
(D-16-25)4cdd . .	Wil 4	550	7.9	22.5	1.606	1.248	.103	.066	1.958	1.016	1.145	.153	.516	-2.99	.058	327
(D-15-25)27cdd . .	Wil 5	1,100	7.8	26.5	2.491	.724	.050	.082	2.219	.451	.500	.068	.665	-2.61	.043	259

\*Calculated.

and a north basin. An estimated 4.6 million acre-ft of recoverable ground water is in storage in the upper 1,500 ft of the aquifer. Annual recharge of an estimated 370 acre-ft indicates long residence time of the water in storage (Matlock, 1981).

Reactions were modeled along a general flow path from the recharge area about 2 mi downgradient to Vek 1 (Vekol 1), 7 mi downgradient to Vek 2, and 8 mi downgradient to Vek 3 near the center of the basin (fig. 15). XRD analyses of the bulk-rock fraction of the basin fill at Vek 3 indicated that labradorite, bytownite, and andesine are present throughout the column, with substantial albite and oligoclase between 1,400 and 1,900 ft. Andesine, augite, and potassium feldspar were selected as the primary reactant minerals. The changes in ground-water chemistry as a function of distance along the flow path are illustrated in figure 16. The phases and mass transfer associated with these changes are shown in table 11.

On the basis of the water composition and selected phases, hydrolysis of augite and andesine and precipitation of calcite are the dominant reactions occurring between recharge and Vek 1 (reaction 1). In contrast to the recharge area, calcite precipitates downgradient. Calcium decreases early along the flow path, primarily because of calcite precipitation but partly because of montmorillonite formation. A significant amount of magnesium, 0.42 mmol, is removed from solution by montmorillonite formation, but presumably it is replenished by weathering of ferromagnesian minerals, whose presence is suggested by an adjacent basalt outcrop. Sodium, sulfate, chloride, and pH increase downgradient between

Vek 1, 2, and 3 (reactions 2 and 3). Alkaline earths are almost wholly depleted downgradient, and bicarbonate decreases to nearly one-third that of the recharge water (reaction 4). Potassium and fluoride show little change downgradient, but fluoride concentrations increase from recharge to require an additional phase, fluorite. Ion exchange of calcium replacing sodium on the substrate, the most likely exchange reaction, accounts for a portion of the calcium and sodium concentrations. Ion exchange and its implication are discussed in detail in the section on "Ion Exchange," where it is postulated that ion exchange does not occur in dilute waters.

The large mass transfer of the ferromagnesian mineral and the large concentration of magnesium in the ground water at Vek 1 point out two significant weathering traits: (1) the high weathering rates of the ferromagnesian minerals in the upgradient portion of the aquifer and (2) the overall high chemical aggressiveness occurring in the aquifer upgradient. CO<sub>2</sub>(aq) decreases from an average concentration of about 0.60 mmol in the recharge area to 0.27 mmol upgradient at Vek 1 to 0.00 mmol downgradient at Vek 3. The decrease in CO<sub>2</sub>(aq) and the high but decreasing weathering rates of the silicates indicate that carbonic acid plays the predominant role in the weathering process and that the residence time of the ground water is less critical. CO<sub>2</sub>(aq) decreases downgradient as hydrogen ions are consumed, and carbonic acid disassociates to form bicarbonate ions that are subsequently precipitated as calcite in response to increases in pH and temperature. The high chemical reactivity of the water and the instability of the ferromagnesian minerals are indicated by the mass transfer of



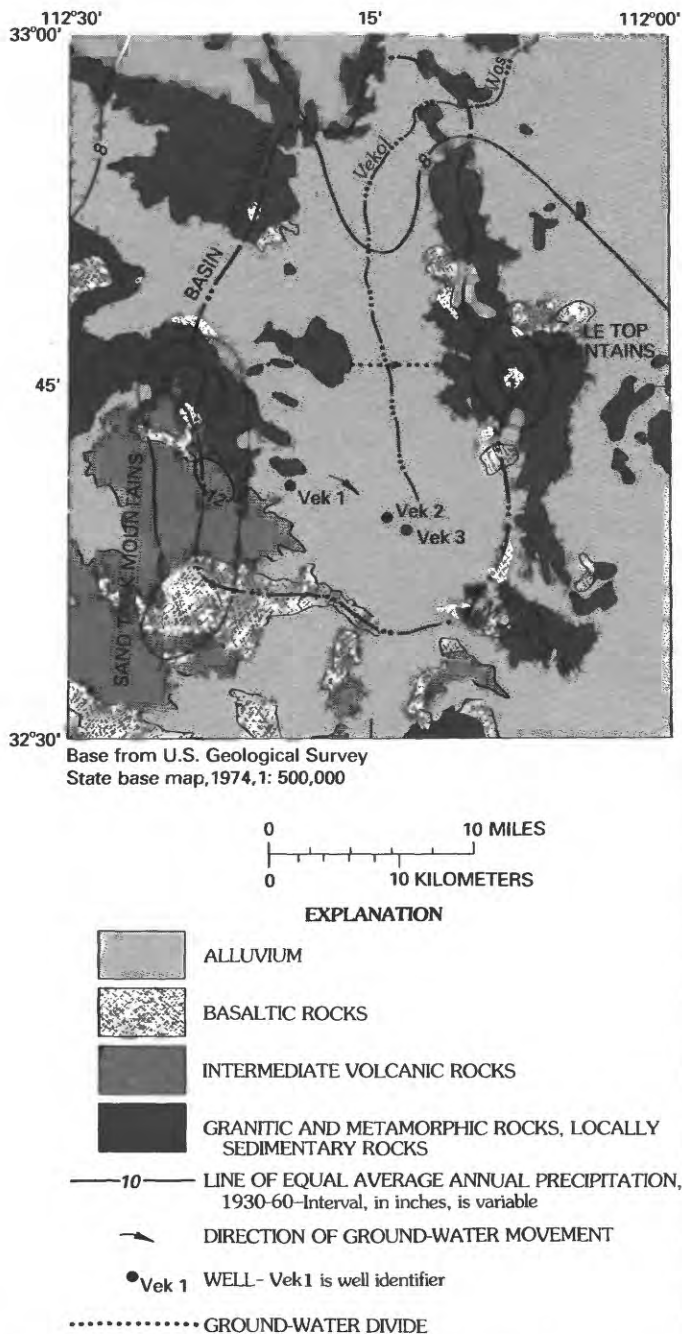


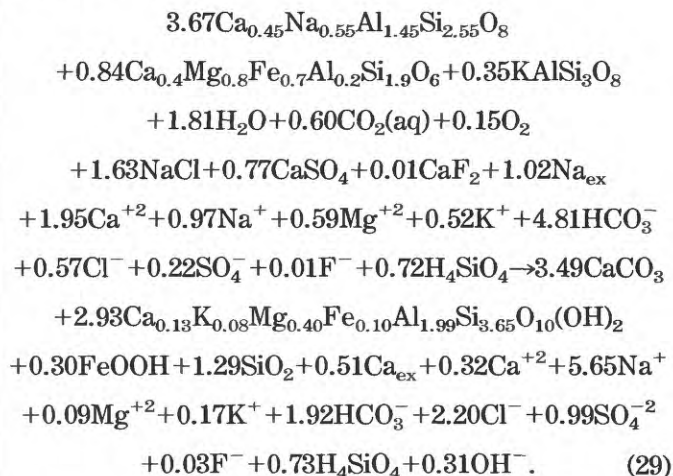
FIGURE 15.—Generalized geology, wells, and ground-water movement in Vekol Valley.

the silicates from recharge to Vek 1; approximately 2.1 mmol of andesine and 0.9 mmol of augite are weathered over the initial distance of 1.8 mi, whereas 4.5 mmol of andesine and 1.2 mmol of augite are weathered over the total distance of about 8 mi.

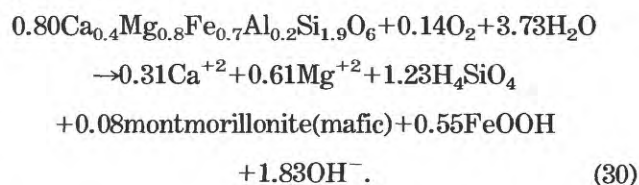
Silicate hydrolysis increases the pH of the water from about 7 in the recharge area to 8 downgradient in spite of calcite precipitation of several millimoles. The precipitation of calcite is an acid-producing reaction and in a sense

can be considered a reverse weathering reaction as  $\text{CO}_2$  and  $\text{H}^+$  are produced (Drever, 1982); it can be written in the reverse of reactions shown in equations 14 and 15. The acid reactions are neutralized by hydroxyl ions produced by silicate hydrolysis per equations 18, 19, and 20.

The summary reaction written to the predominant dissolved species from the recharge area along the flow path to Vek 3 is



Conservation of electrons as well as of mass is maintained along the flow path from recharge to Vek 3. Assuming that iron is  $\text{Fe}^{+2}$  in augite and  $\text{Fe}^{+3}$  in montmorillonite and that dissolved oxygen is the oxidant, the oxidation of iron and the hydrolysis of about 0.80 mmol of augite along the flow path can be written to oxygen and water:



The electron-balanced equation shows that 0.14 mmol of oxygen is being consumed, which, with an initial concentration of about 9 mg/L (0.28 mmol/L) extrapolated from data in figure 7, would deplete dissolved oxygen to about 4.5 mg/L at Vek 3 (well E in fig. 7), close to the measured concentration of 4.3 mg/L.

The higher weathering rate of the ferromagnesian minerals relative to the plagioclase is supported by the XRD analysis of the basin fill at Vek 3. XRD analyses show that plagioclase is present in trace to small amounts in the less than 2- $\mu\text{m}$  fraction and, along with quartz, calcite, and potassium feldspar, is dominant in the less than 62- $\mu\text{m}$  fraction. Amphiboles and pyroxenes were not detected in the less than 2- $\mu\text{m}$  fraction and only rarely in the less than 62- $\mu\text{m}$  fraction. The decrease in

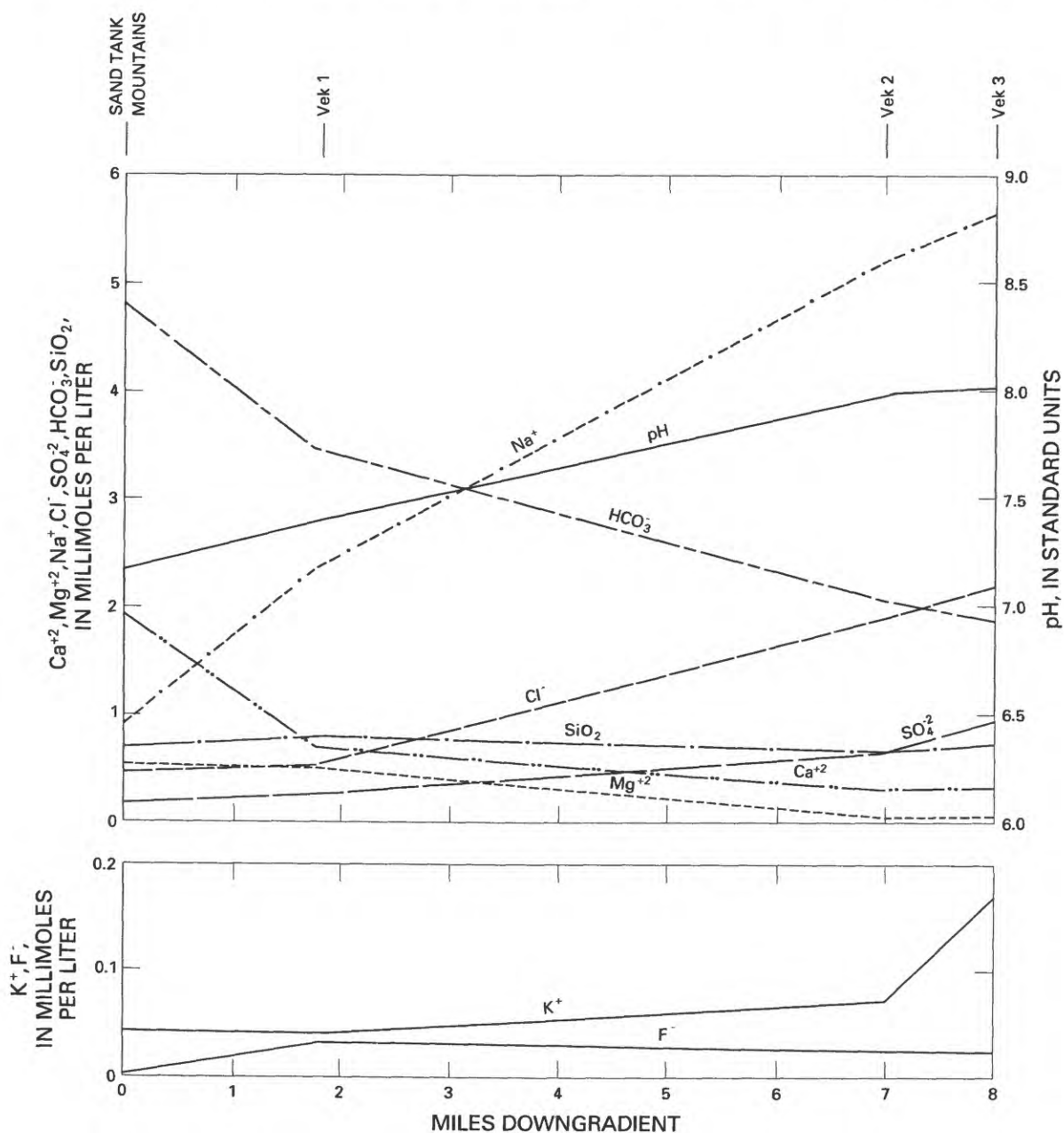


FIGURE 16.—Changes in concentration of dissolved chemical constituents along the flow path in Vekol Valley. (Well locations shown in fig. 15.)

the weathering of mafic minerals relative to that of plagioclase may explain why the existing ground water tends to maintain its oxidizing character for an indefinite period.

The saturation indices of the ground water with respect to selected mineral phases are shown in table 12. The saturation state of the ground water is consistent with the weathering and precipitation reactions and with the minerals observed and postulated in the basin fill. Along the flow path, the ground water maintains equilibrium with respect to calcite but becomes increasingly

undersaturated with respect to dolomite. The water becomes slightly less undersaturated but is still highly undersaturated with respect to the ferromagnesian minerals clinoenstatite and diopside. The water is saturated with respect to potassium feldspar and, as determined in the recharge area, is supersaturated with respect to clay minerals, iron oxides, zeolites, and quartz minerals. Poor aluminum data again may be the cause of the apparent supersaturation of the clay minerals. The water appears to be near equilibrium with respect to muscovite. Muscovite is present in the less than 62- $\mu\text{m}$  and less than



TABLE 11.—*Summary of mass transfer for Vekol Valley*  
 [Values\* in millimoles per kilogram H<sub>2</sub>O; well names keyed to fig. 15; Vek, Vekol Valley]

Phases	Reaction number and flow path			
	1 Recharge to Vek 1	2 Vek 1 to Vek 2	3 Vek 2 to Vek 3	4 Recharge to Vek 3
O <sub>2</sub> .....	0.09	0.05	0.01	0.15
CO <sub>2</sub> .....	.33	.25	.02	.60
Calcite .....	-1.58	-1.73	-.18	-3.49
Andesine (An <sub>45</sub> ) .....	1.33	2.33	.01	3.67
Potassium feldspar .....	.06	.17	.09	.32
Augite .....	.51	.28	.05	.84
Silica .....	-.63	-.44	-.17	-1.24
Halite .....	.02	1.33	.28	1.63
Gypsum .....	.05	.48	.24	.77
Fluorite .....	.01	.00	.00	.01
Montmorillonite (mafic) ..	-1.06	-1.82	-.04	-2.92
Goethite .....	-.25	-.02	-.02	-.29
Ion exchange** .....	.35	.09	.08	.52

\*Reactants are positive and products are negative.

\*\*Calcium replacing sodium on the substrate.

2- $\mu$ m fractions of the basin fill and appears to be an inert mineral downgradient as well as in the recharge area. Apparently, owing to the stability of muscovite, any formation of a new mineral may not involve breakdown of the lattice structure but may involve only ionic substitution in the original sheet structure.

The trilinear plot in figure 17 illustrates the evolution of the recharge water from the calcium and bicarbonate apexes toward the sodium and chloride sulfate apexes. The plot indicates that early along the flow path, as

interpreted from the small sulfate and chloride concentrations, the ground water evolves into an intermediate sodium magnesium calcium bicarbonate type or a sodium calcium magnesium bicarbonate type owing to enrichment of magnesium relative to calcium. The trend is an apparent result of the concurrent reactions of calcite precipitation and the weathering rates of the ferromagnesian minerals relative to plagioclase as determined by the modeling.

The trends in chemistry in Vekol Valley depicted in figures 16 and 17 are observed in all dilute ground waters that evolve under closed conditions throughout the Basin and Range lowlands province. The similarities are immediately apparent in figure 18, which shows chemical trends for Butler, McMullen, lower San Pedro, and San Simon Valleys and the Big Sandy and Safford basins. These chemical trends need not be invariably similar and may differ markedly in some basins. Modeling of lower San Pedro Valley, McMullen Valley, and Ranegras Plain will demonstrate that regardless of differences in water chemistry, the reactions and mass transfer of many phases are indeed virtually invariant.

#### LOWER SAN PEDRO VALLEY

Lower San Pedro Valley is a long, narrow, northwest-trending basin in semiarid southeastern Arizona where ground water occurs under confined conditions. The basin is structurally and hydrologically typical of several elongated basins in the southeastern and northwestern parts of the study area, some of which contain major

TABLE 12.—*Saturation indices of the ground water in Vekol Valley with respect to various minerals*  
 [Vek, Vekol Valley; well locations shown in fig. 15. Phases and thermodynamic data from Ball and others (1980). Dashes indicate values not calculated]

Phases	Vek 1	Vek 2	Vek 3	Number of samples	Saturation indices for basin		
					Maximum	Minimum	Average
Adularia .....	—	—	0.489	3	0.489	-0.027	0.160
Albite .....	—	—	-.422	3	-.422	-.929	-.693
Beidellite .....	—	—	1.49	3	.27	-.57	.397
Calcite .....	-0.057	-.088	-.158	11	.238	-.158	.039
Chalcedony .....	.298	.201	.254	11	.341	.133	.224
Clinoenstatite .....	-2.502	-2.856	-2.183	2	-1.721	-3.334	-2.615
Diopside .....	-2.316	-1.414	-1.243	8	-1.243	-3.352	-2.217
Dolomite .....	-.121	-1.838	-.759	11	.053	-1.838	-.345
Fluorite .....	-1.451	-2.185	-2.122	11	-.402	-2.185	-1.506
Goethite .....	—	—	6.868	—	—	—	—
Gypsum .....	-2.237	-2.477	-2.054	8	-1.986	-3.792	-2.411
Halite .....	-7.525	-6.566	-6.596	—	—	—	—
K-mica .....	—	—	0.015	3	.110	-.468	-.114
Montmorillonite CA....	—	—	1.308	3	1.904	.888	1.367
Montmorillonite BF....	—	—	6.044	2	6.044	5.161	5.602
Montmorillonite AB....	—	—	5.352	4	5.352	4.573	4.962
Tremolite .....	—	—	4.298	1	4.298	4.298	4.298

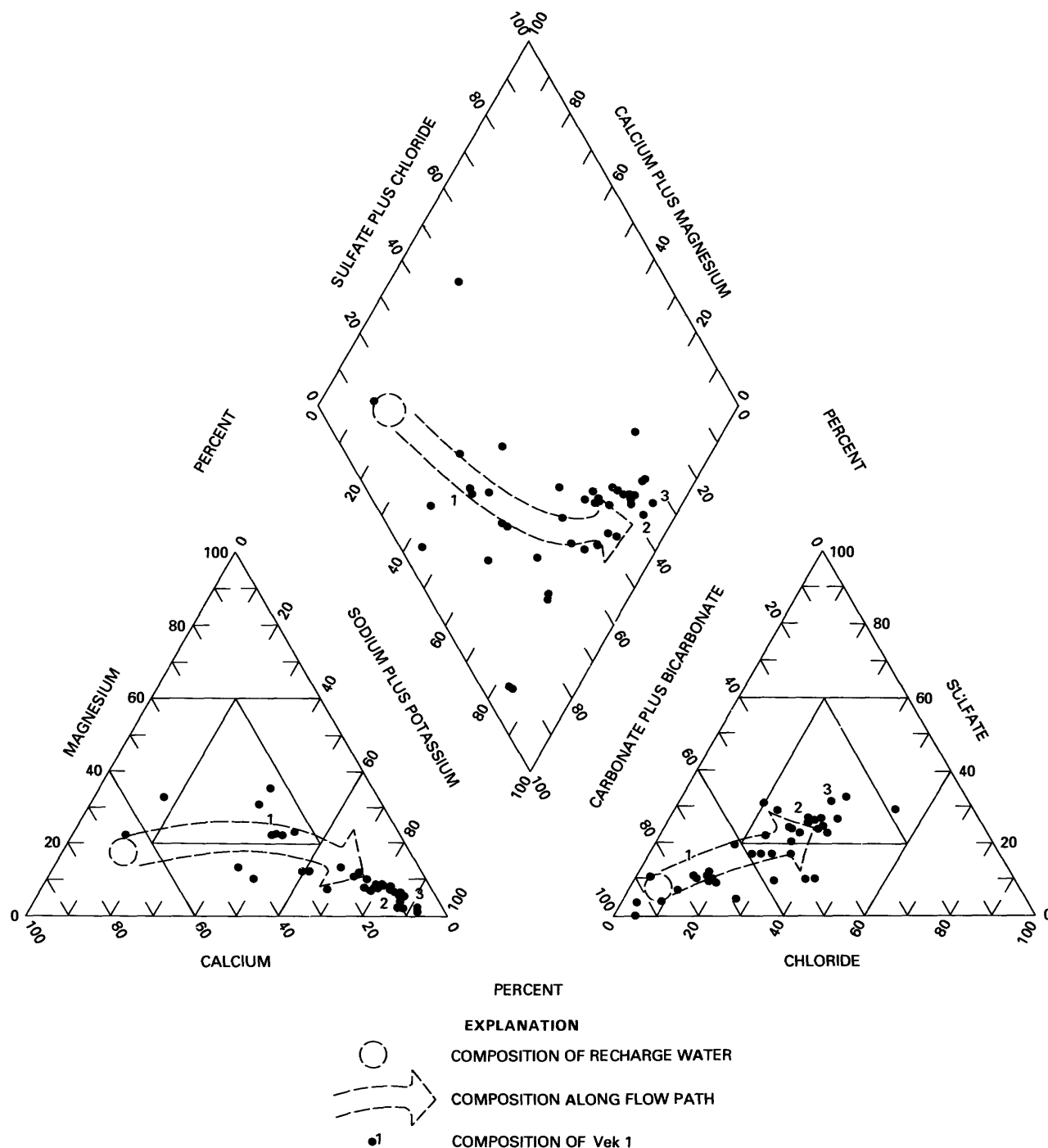


FIGURE 17.—Relative compositions of ground water in Vekol Valley, in equivalent percents. (Well locations shown in fig. 15.)

stream systems. The valley is 65 mi long and 15 to 20 mi wide and extends from the Narrows to Winkelman, where the San Pedro River joins the Gila River (fig. 19). The basin is bounded on the west by granite of the Tortilla Mountains and by gneiss and granite of the Santa Catalina Mountains, and on the east wholly by intermediate and silicic volcanic rocks of the Galiuro Mountains

(Wilson and others, 1969). The basin fill consists mainly of lower basin-fill deposits; most of the upper basin fill has been removed by late Cenozoic uplift and valley erosion. The aquifer consists of coarse-grained deposits of the lower basin fill overlain by a fine-grained confining unit. In a large area extending about 20 mi from Redington to Mammoth, the ground water occurs under

confined conditions at depths of 300 ft near Redington to 1,400 ft near Mammoth. Artesian pressure is sufficient for wells to flow at rates of about 10 to 500 gal/min in this area. Confined conditions are known to exist an additional 10 mi north of Mammoth, but no flowing wells are reported. The flood-plain deposits along the San Pedro River and the stream alluvium along its tributaries consist of mixtures of sand, gravel, and silt and also constitute an important local aquifer (Roeske and Werrell, 1973).

Ground water in lower San Pedro Valley, as indicated by water-level data, is recharged by precipitation and runoff along the Galiuro, Tortilla, and Santa Catalina Mountains and moves toward the basin axis (Roeske and Werrell, 1973). The water chemistry clearly indicates that the ground water of the confined aquifer originates near the Galiuro Mountains and not in the Santa Catalina Mountains on the west side of the valley. The similarity in concentrations of major elements and the large fluoride concentrations of the geochemically closed confined aquifer and wells sampled between the San Pedro River and the Galiuro Mountains are cited as evidence. These waters stand out in contrast to the different major element chemistry, the lower ground-water temperatures, and the small fluoride concentrations of the open system draining the Santa Catalina Mountains. The confined aquifer offers an excellent opportunity to define the mass transfer along a distinct flow path of known origin.

Reactions were modeled along two flow paths from the Galiuro Mountains to the axis of the basin. One flow path is from the mountains to well LSP 1 (lower San Pedro 1) upvalley at the beginning and shallowest part of the confined aquifer. The other flow path is from the mountains to well LSP 2 (well M in fig. 7) downvalley at the deepest point. LSP 1, near Redington, is 387 ft deep and flows at about 15 gal/min. The top of the aquifer is at 370 ft and is overlain by about 360 ft of fine-grained sediments. The ground water is highly dilute, indicating an absence of the gypsiferous deposits within the aquifer found elsewhere in the basin. The recharge area is about 7 to 8 mi eastward, normal to the axis of the valley. LSP 2, near Mammoth, is 1,485 ft deep and flows at about 50 gal/min. The flow path of 7 to 8 mi is similar in distance to the flow path to LSP 1, but the aquifer is situated considerably deeper, and the ground water is higher in dissolved solids. The lithologic log of LSP 2 indicates that the top of the aquifer is at about 1,370 ft below land surface, underlying fine-grained gypsiferous and red clay deposits. Examination of the red clay reported by drillers in the area shows that the clay is entirely of "water worn particles of volcanic rocks" (Halpenny and others, 1952, p. 89). The chemistries along both flow paths are shown in figure 20.

The reactant phases were selected through a review of the published literature (Creasey, 1965; Krieger, 1979, 1980) on the mineralogy of the Galiuro Mountains. Biotite and hornblende are both found in the rhyolitic tuffs. Krieger (1979) did not detect biotite in 22 of 62 samples of the tuffs but did detect trace amounts in the remaining samples. Hornblende was detected in 15 of the samples; some was visible in hand specimens. Hornblende was selected because it is the more common ferromagnesian mineral in andesite, the other dominant rock type of the Galiuro Mountains, and in granodiorite and diabase found throughout the valley (Creasey, 1965). The phases and the mass transfer along the flow paths are shown in table 13.

Reaction 1 in table 13 shows that the mass transfer of most phases along the flow path from the recharge area to LSP 1 is similar to the mass transfer derived for Vekol Valley. The mass transfer of the silicates, in particular, is markedly similar. The major differences in water chemistries between the two basins can be attributed to the dissolution of the soluble components of halite and gypsum. Ion exchange of calcium for sodium—again the most likely exchange reaction—does not appear to be occurring and is interpreted to be a result of the dilute waters.

Reaction 2 describes the mass transfer along a similar flow path from the Galiuro Mountains to LSP 2, located approximately 17 mi downvalley. Reactant phases used in the modeling of LSP 1 were selected for LSP 2 on an assumed homogeneity of the geology of the Galiuro Mountains. The mass transfer of most phases along the flow path from the recharge area to LSP 2 (reaction 2) is similar to that determined near the origin of the aquifer system near Redington (reaction 1). Significant differences lie only in the greater mass transfer of gypsum and, consequently, the presumed presence of ion-exchange reactions. The similarity in the mass transfer of the silicates supports the assumed homogeneity of the source rock and the transferability of the reactions. A slightly greater mass transfer of andesine (0.18 mmol) and hornblende (0.01 mmol) may be due to greater hydrolysis as a result of deep circulation and higher temperature (42 °C). Similarly, the greater amount of calcite precipitated (0.57 mmol) also may be related to these variables, particularly temperature.

Reactions 2 and 3 suggest that ion exchange of calcium for sodium is occurring. The analytical data in table 10 show that the ground water in the downvalley well (not downgradient), well LSP 2, contains appreciably more sodium than that in the upvalley well, well LSP 1 (5.65 and 2.78 mmol, respectively). The increase in sodium could be interpreted to be a result of additional weathering reactions because the difference in mass transfer of halite between the two waters is smaller than the difference in molar sodium concentrations and because

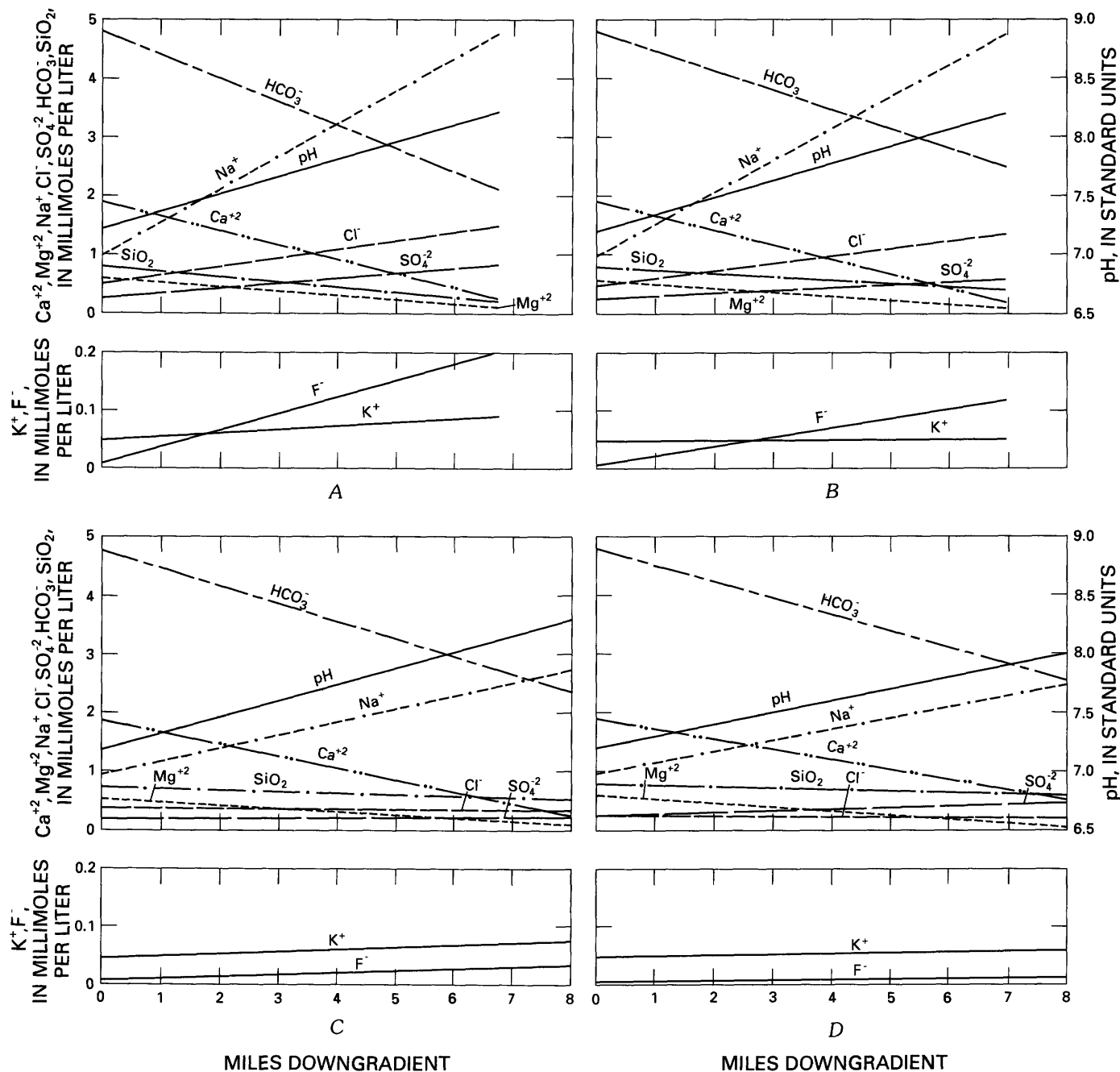


FIGURE 18.—Changes in concentration of dissolved chemical constituents along flow paths in selected basins in the Basin and Range lowlands. A, Butler Valley; B, McMullen Valley; C, lower San Pedro Valley; and D, San Simon Valley. (Continued on next page.)

the downvalley well has the larger concentrations. The general agreement of the silicate mass transfer accompanied by the mass transfer of halite and gypsum derived between the final water compositions in the upvalley and downvalley wells implies that differences in sodium concentrations are best explained by ion exchange and not by continued hydrolysis.

Reaction 4 shows the mass transfer derived to LSP 1 using biotite, the other pertinent ferromagnesian min-

eral in the Galiuro volcanic complex, as a reactant. The use of biotite as an alternate source of magnesium results in significant ion exchange of sodium exchanging for calcium. Ion exchange of monovalent sodium for divalent calcium in the dilute waters is unlikely, and reaction 4 is not a realistic alternative.

The hydrolysis of hornblende and the oxidation of iron are written analogously to the hydrolysis and oxidation of augite. The hydrolysis of hornblende along both flow

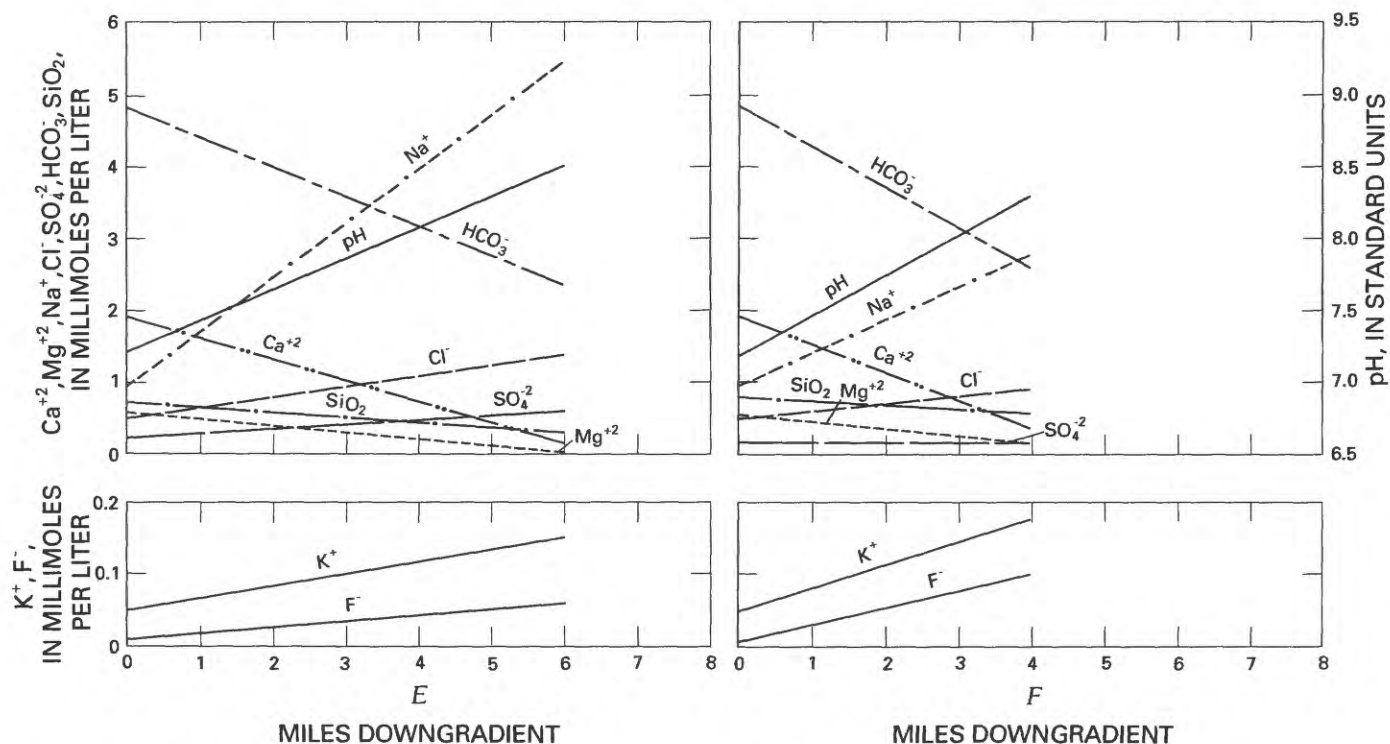
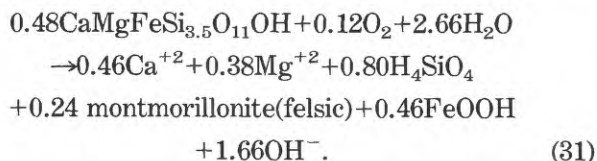


FIGURE 18.—Changes in concentration of dissolved chemical constituents along flow paths in selected basins in the Basin and Range lowlands. *E*, the Big Sandy basin; and *F*, the Safford basin.

paths is approximately 0.48 mmol, which results in consumption of 0.12 mmol of dissolved oxygen:

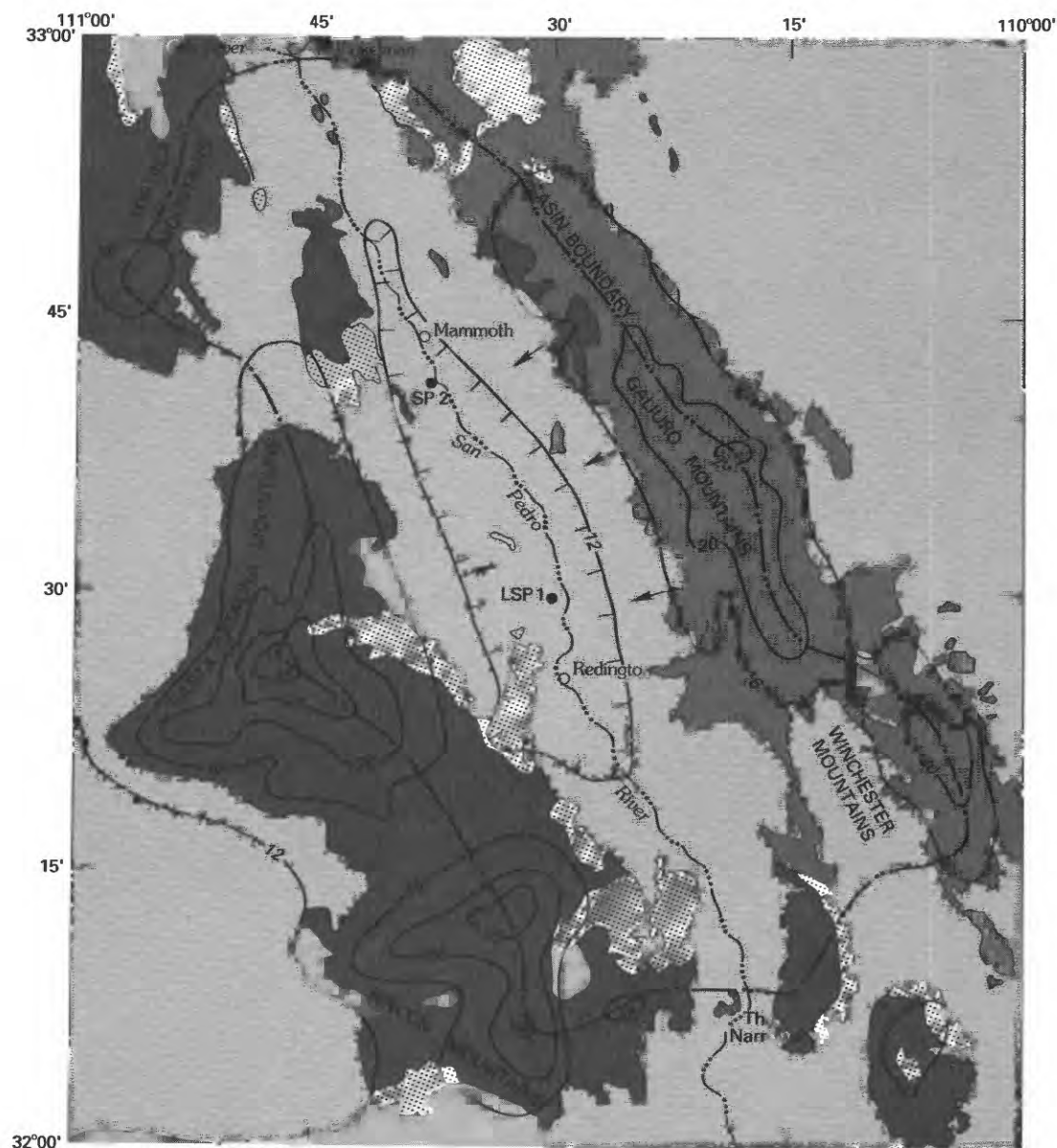


The saturation state of the ground water with respect to most minerals (table 14) is in general agreement with the derived mass transfer. The ground water is undersaturated with respect to dolomite, plagioclase, the ferromagnesian minerals, and, in contrast to the ground water in Vekol Valley, to potassium feldspar. The ground water is slightly supersaturated with respect to chalcedony and is highly supersaturated with respect to goethite and most of the clay minerals. The water is undersaturated at LSP 1 but saturated at LSP 2 with respect to fluorite. Fluoride concentrations in the artesian aquifer of lower San Pedro Valley are some of the largest in the study area.

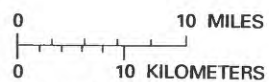
Surprisingly absent from the ground water are the large silica concentrations normally associated with the weathering of welded tuffs and silicic volcanic rocks. Analyses of ground water from volcanic and welded tuff terranes in Nevada show that the ground water contains considerably larger silica concentrations (Winograd,

1971; White, 1979). Concentrations in wells sampled in the artesian aquifer along the San Pedro River and between the river and the Galiuro Mountains do not indicate large silica contents but are comparable to concentrations found in other terranes. The reasons for these differences are unclear.

The nearly identical mass transfer of the silicates determined along the two flow paths 17 mi apart and the negligible mass transfer for the flow downvalley clearly show that no reactions are occurring and suggest that little or no water is moving downvalley. Precipitation apparently recharges the aquifer near the Galiuro Mountains, moves toward the center of the basin, and discharges near the San Pedro River. The presence of a dense mesquite forest along the axis of the basin is indicative of large evapotranspiration losses. Measurements of  $^{14}\text{C}$  specific activity and of tritium strongly support the modeling conclusions of little downvalley movement of water. Specific activity is a measure of the extent of the radioactive decay of  $^{14}\text{C}$ , the radiogenic isotope of carbon, and of any addition of nonradiogenic carbon; it is expressed as a percent of the  $^{14}\text{C}$  that has not undergone any radioactive decay, usually considered to be 100 PMC (percent modern carbon) (Fontes and Garnier, 1979). The  $^{14}\text{C}$  activity of about 20 PMC for the tritium-free waters and similar  $^{13}\text{C}$  content at LSP 1 and LSP 2 would give nearly identical corrected ages under



Base from U.S. Geological Survey  
State base map, 1974, 1:500,000



#### EXPLANATION








- |   |   |   |   |
|---|---|---|---|
|  | ALLUVIUM                                |  | LINE OF EQUAL AVERAGE ANNUAL PRECIPITATION, 1930-60—Interval in inches, is variable |
|  | INTERMEDIATE AND SILICIC VOLCANIC ROCKS |  | DIRECTION OF GROUND-WATER MOVEMENT  |
|  | SEDIMENTARY ROCKS                       |  | WELL—LSP1 is well identifier  |
|  | GRANITIC AND METAMORPHIC ROCKS          |   |   |

FIGURE 19.—Generalized geology, wells, and ground-water movement in lower San Pedro Valley.



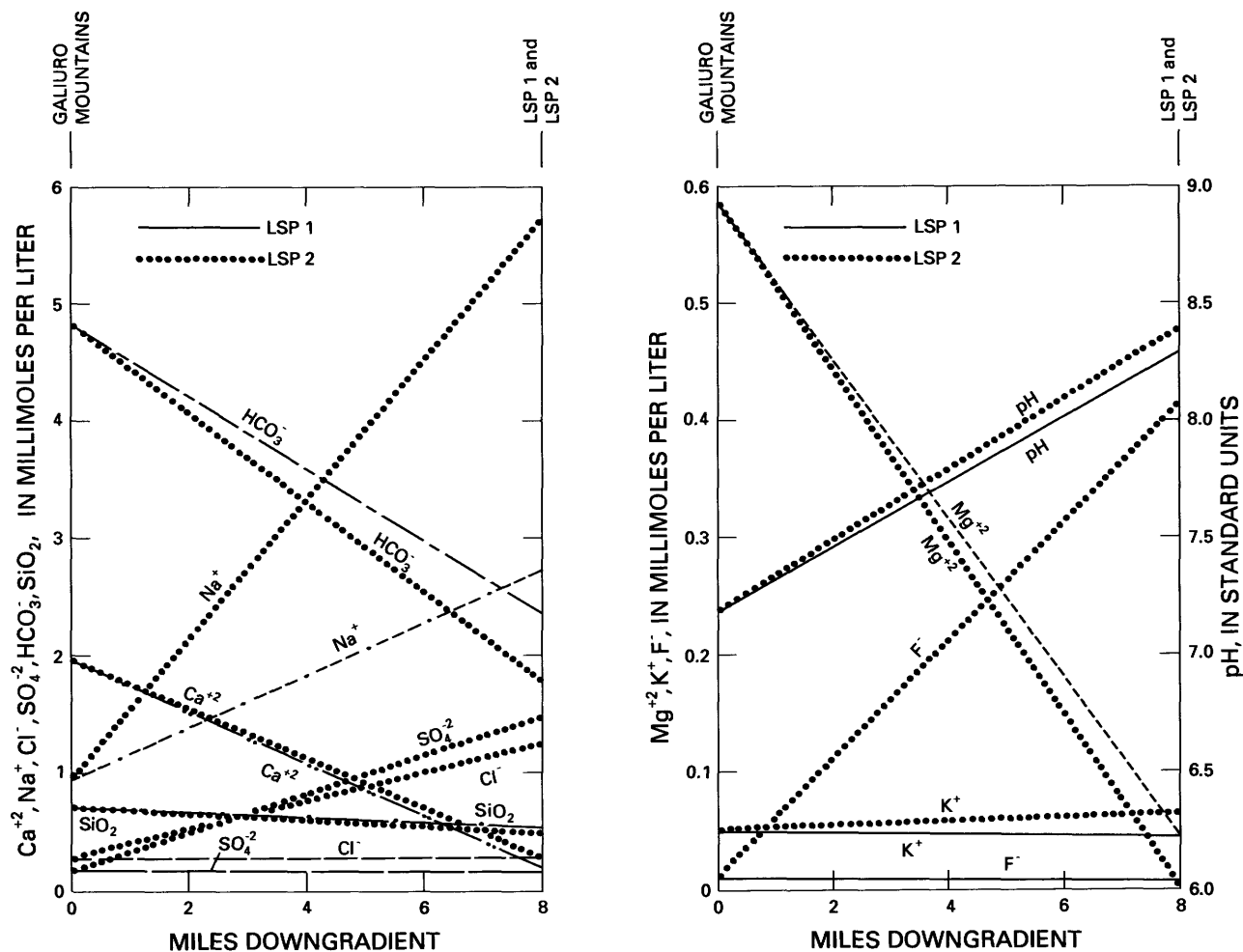


FIGURE 20.—Comparison of ground-water compositions along the flow paths in lower San Pedro Valley. (Well locations shown in fig. 19.)

presumed identical correction factors indicated by the mass transfer. Ground-water movement in the lower San Pedro Valley formerly was characterized as moving from the mountains toward the basin axis and downvalley (Halpenny and others, 1952; Roeske and Werrell, 1973), a direction that is not supported by the geochemical model.

The similarity in the mass transfer of the silicate phases in the water-table aquifer of Vekol Valley and the confined aquifer of lower San Pedro Valley (mass transfer of plagioclase for the four downgradient wells is  $3.52 \pm 0.19$  mmol) suggests that the aquifers are similar closed systems. The agreement clearly indicates that in Vekol Valley ground water is being recharged along the mountain front and virtually no precipitation or runoff recharges the aquifer along the valley floor. As demonstrated later in modeling the Willcox basin, satisfactory mass transfer cannot be derived for the evolution of the

ground water if the system is open to  $\text{CO}_2$  and additional recharge.

#### RANEGRAS PLAIN

Ranegras Plain is a moderately large basin about 50 mi long and 20 mi wide in arid western Arizona that contains ground water of relatively high salinity (fig. 21). The rock types of the mountains surrounding the basin are similar to those in Vekol Valley; unlike Vekol Valley, however, the basin fill contains evaporites near the surface that are responsible for the high salinity (table 10). The basin is bounded on the east by basalt and granite of the Little Harquahala Mountains and granite of the Granite Wash Mountains; on the south by basalt and andesite of the Little Horn, Eagle Tail, and Kofa Mountains; and on the west and north by andesite of the Plomosa and New Water Mountains and andesite and granite of the Bouse Hills (Wilson and others, 1969).

TABLE 13.—*Summary of mass transfer for lower San Pedro Valley*  
[Values\* in millimoles per kilogram H<sub>2</sub>O; LSP, lower San Pedro Valley; well names keyed to fig. 19. Dashes indicate phase not used]

Phases	Reaction number and flow path			
	1 Recharge to LSP 1	2 Recharge to LSP 2	3 LSP 1 to LSP 2	4 Recharge to LSP 1
O <sub>2</sub> .....	0.12	0.12	0.00	0.17
CO <sub>2</sub> .....	.57	.59	.02	.57
Calcite.....	-3.01	-3.58	-.57	-3.01
Andesine (An <sub>33</sub> ).....	3.16	3.34	.18	3.92
Potassium feldspar.....	.32	.36	.04	.39
Hornblende.....	.46	.47	.01	—
Biotite.....	—	—	—	.45
Silica.....	-1.99	-2.13	-.14	-2.01
Halite.....	.00	.67	.67	.00
Gypsum.....	.00	1.24	1.24	.00
Fluorite.....	.05	.20	.15	.05
Montmorillonite (felsic)..	-2.50	-2.65	-.15	-3.04
Goethite.....	-.20	-.21	-.01	-.37
Ion exchange**.....	.00	.88	.88	-.28

\*Reactants are positive and products are negative.

\*\*Calcium replacing sodium on the substrate.

The aquifer throughout most of the basin consists of sand and gravel of the lower basin fill that are partially overlain by an areally extensive fine-grained unit. The fine-grained unit extends to the west from the basin center midway to the Bear Hills, to the north nearly to the Bouse Hills, to the east to the basalt flows adjacent to the Little Harquahala Mountains, and to the south for an undetermined distance probably covering much of the southern part of the basin. The fine-grained unit is about

500 to 600 ft thick in the central part of the basin near Bear Hills and contains evaporites in the lower part. Predevelopment and present (1981) depths to water in the center of the basin were about 120 ft.

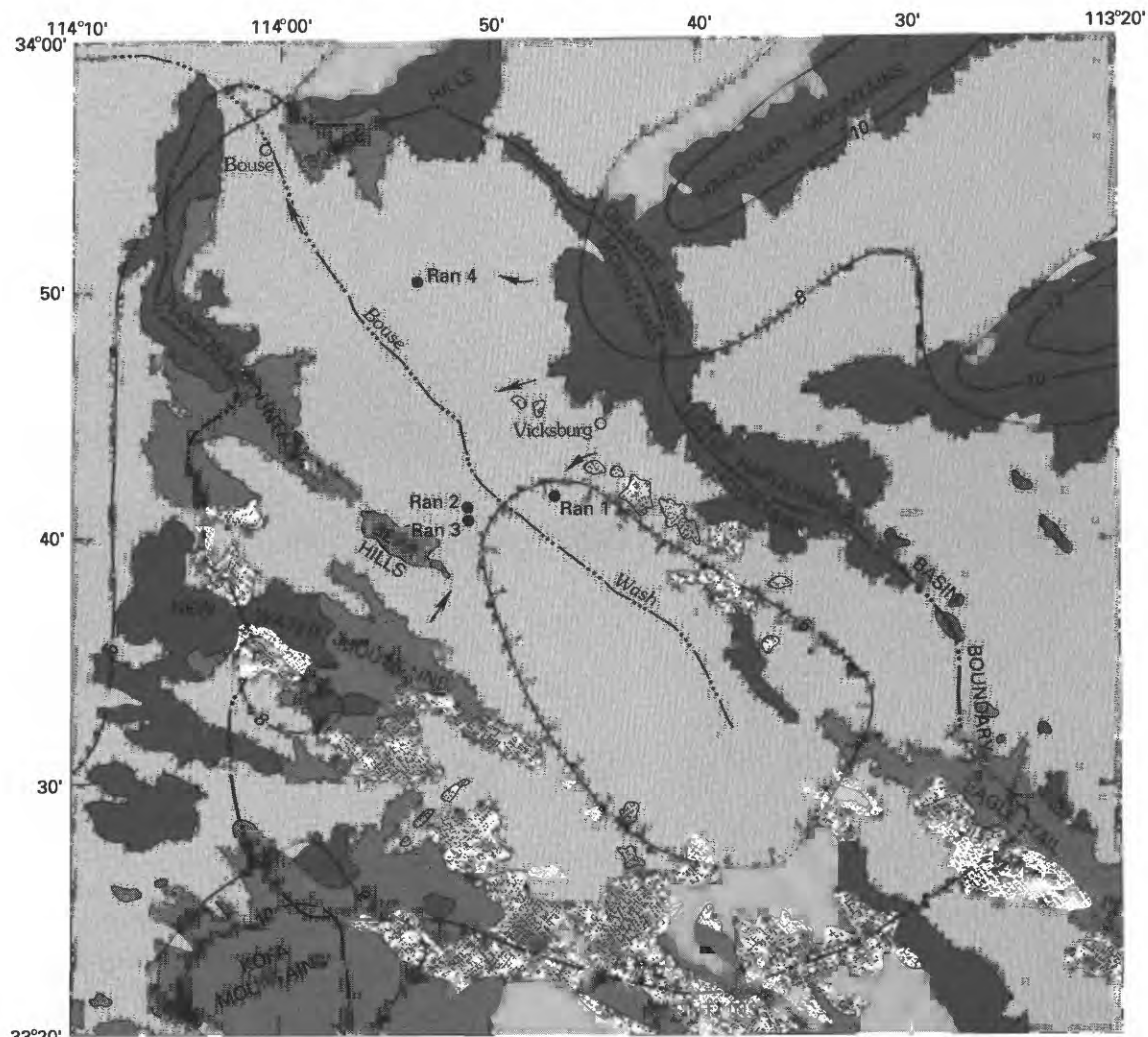
The major recharge area for the basin is adjacent to the Little Harquahala and Granite Wash Mountains owing to the greater precipitation relative to that in adjacent mountains. The Plomosa and New Water Mountains to the west, although smaller in area and lower in altitude, receive significant precipitation and probably also contribute recharge. The Kofa Mountains in the southwest also may contribute significant recharge to the basin, although much of the area drains to the south. Briggs (1969) indicated that water movement is from southeast to northwest throughout the basin, but owing to the scarcity of water-level data for the southern part of the basin and the flatness of the potentiometric surface determined from available water-level data, areas of recharge and the direction of ground-water movement are poorly defined. Indeed, the  $\delta D$  and  $\delta^{18}O$  data suggest that some ground water may be moving to the south. An estimated 10 million acre-ft of water is in storage, and average annual recharge to the basin is estimated to be 500 to 1,500 acre-ft (Briggs, 1969).

The ground water throughout much of the basin is not suitable for all purposes. The water contains dissolved-solids concentrations greater than 3,000 mg/L and large concentrations of trace elements. Arsenic, boron, chromium, fluoride, and selenium occur naturally and commonly exceed the maximum contaminant level for these constituents. The ground water evolves from a sodium

TABLE 14.—*Saturation indices of the ground water in lower San Pedro Valley with respect to various minerals*

[LSP, lower San Pedro Valley; well locations shown in fig. 19. Phases and thermodynamic data from Ball and others (1980). Dashes indicate values not calculated]

Phases	LSP 1	LSP 2	Number of samples	Saturation indices for basin		
				Maximum	Minimum	Average
Adularia.....	0.185	-1.186	4	0.487	-1.186	-0.449
Albite.....	-.586	-1.614	4	.295	-1.614	-1.101
Beidellite.....	1.572	—	4	1.572	-.574	.635
Calcite.....	-.022	.154	8	.321	-.022	.126
Chalcedony.....	.262	.064	8	.315	.064	.213
Clinoenstatite.....	-2.490	-2.849	2	-2.490	-2.849	-2.670
Diopside.....	-1.511	-1.243	—	—	—	—
Dolomite.....	-.691	-1.564	8	.532	-1.564	-.889
Fluorite.....	-.860	-.132	8	.459	-.860	-.290
Goethite.....	6.464	—	3	6.801	5.623	6.296
Gypsum.....	-2.765	-2.036	8	-1.689	-2.765	-2.226
Halite.....	-7.708	-6.857	—	—	—	—
K-mica.....	-.270	-3.866	4	-.043	-3.866	-2.447
Montmorillonite CA.....	1.389	-1.828	3	1.512	-1.828	-.358
Montmorillonite BF.....	4.864	—	2	4.864	4.517	4.691
Montmorillonite AB.....	4.265	—	1	3.958	3.958	3.958
Tremolite.....	3.402	1.823	2	3.402	1.823	2.613



0 10 MILES  
0 10 KILOMETERS

## EXPLANATION





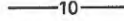


-  ALLUVIUM
-  BASALTIC ROCKS
-  INTERMEDIATE VOLCANIC ROCKS
-  GRANITIC AND METAMORPHIC ROCKS,  
LOCALLY SEDIMENTARY ROCKS
-  —10— LINE OF EQUAL AVERAGE ANNUAL PRECIPITATION,  
1930-60—Interval, in inches, is variable
-  DIRECTION OF GROUND-WATER MOVEMENT
-  ● Ran 1 WELL—Ran 1 is well identifier

FIGURE 21.—Generalized geology, wells, and ground-water movement in Ranegras Plain.

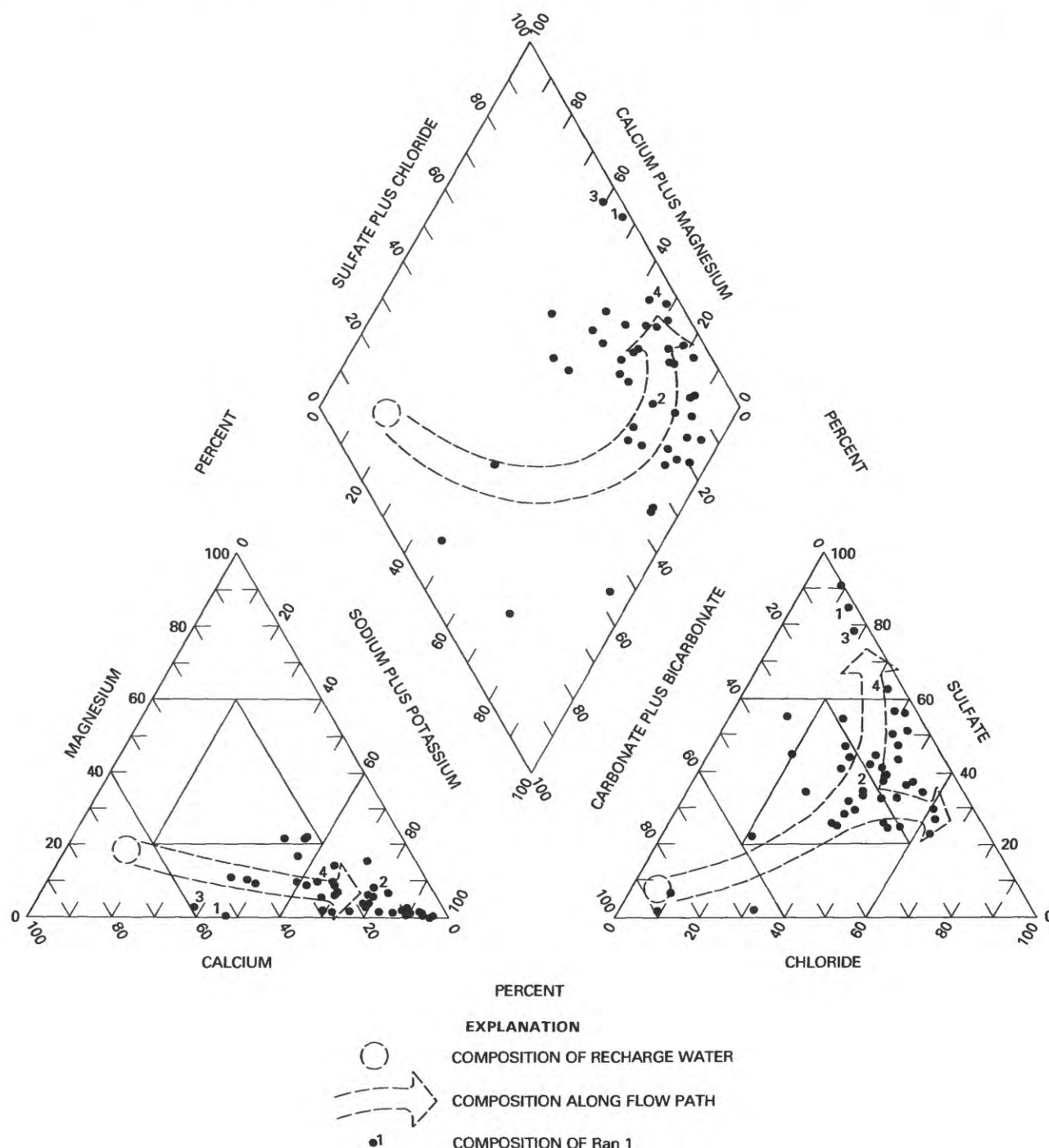


FIGURE 22.—Relative compositions of ground water in Ranegras Plain, in equivalent percents. (Well locations shown in fig. 21.)

mixed-anion type near the basin margins, where dissolved-solids concentrations range between 500 and 1,000 mg/L, to a sodium chloride sulfate or sodium sulfate chloride type toward the basin interior, where concentrations range between 1,000 and 3,000 mg/L. The trilinear plot in figure 22 shows the evolutionary path of the ground water from a bicarbonate type to chloride and

sulfate types. Mesozoic sedimentary rocks that crop out near the Harcuvar and Granite Wash Mountains and Mesozoic and Paleozoic sedimentary rocks in the Little Harquahala Mountains may be sources of the large sulfate and chloride concentrations.

Reactions were modeled along flow paths between the Little Harquahala and Granite Wash Mountains to Ran 1

(Ranegras 1), a well near the depositional center of the basin, and between the Plomosa and New Water Mountains to Ran 2 and 3 near the center of the basin. The selected paths probably are representative of the direction of flow; waters originating as recharge on both flanks move toward the center of the basin. Recent water-level and stable-isotope data obtained during this study support this direction of flow in the east recharge area.

The changes in ground-water chemistry downgradient from the east and west recharge areas to the center of the basin are shown in figure 23. The changes in composition along both flow paths are markedly different from the changes observed along the flow paths in Vekol Valley and lower San Pedro Valley. The compositions generally are higher in calcium, sodium, sulfate, and chloride and are lower in bicarbonate. In view of the large areal extent and diversity of physiography of the study area, differences in chemistry may be caused by several factors, such as (1) occurrence of additional reactions, (2) occurrence of similar reactions but with different minerals or mineral compositions, or (3) differences in the mass transfer of the silicates, halite, or gypsum.

The summary of mass transfer for Ranegras Plain is shown in table 15. The silicate phases used for Vekol Valley were adopted for Ranegras Plain because of the similarity in geology between the two basins, as the south-central areas of both basins are bounded by andesite and basalt. Reaction 1 shows that along the flow path from the east recharge area to Ran 1, identical reactions and virtually identical mass transfer of the silicate phases are occurring in Ranegras Plain and Vekol Valley, in spite of the considerable differences in water chemistry. Differences in chemistry to Ran 1 can be explained by simple dissolution of gypsum and halite and modification by an additional reaction, ion exchange. Calcium exchanging for sodium apparently is occurring in Ranegras Plain and thus is a highly significant reaction in controlling the sodium and calcium concentrations in the ground water. The calcium and sulfate concentrations and the additional ion-exchange reaction and its mediating effect on the chemistry are reflected in the trilinear plot (fig. 22). The orderly sequence of the evolution of dilute waters downgradient toward the sodium and sulfate apexes are not as apparent.

Figure 24 and reaction 2 in table 15 show the changes in chemistry and mass transfer along the flow path from the west recharge area to Ran 2. In spite of differences in chemistry between Ran 1 and Ran 2, the mass transfer of most phases at Ran 2 are again markedly similar to those determined along the flow path to Ran 1. The differences are attributed largely to a greater mass transfer of gypsum and calcite. The similarity of the mass

transfer of the silicates provides a decisive factor for the validity of transferability of reactions. The validity is based on the assumption that the kinetics of the silicates are invariant in ground water under identical hydrologic and temperature conditions and mineral environments. The total mass transfer of the aluminosilicates of 5.09 and 5.01 mmol and the mass transfer of augite of 0.86 and 0.93 mmol for Ran 1 and Ran 2, respectively, attest to the similarity and transferability of reactions within the basin.

The mass transfer derived along the flow path from the west recharge area to Ran 3 (reaction 3), however, is unlike that determined for Ran 2 and in the initial analysis does not support the transferability of reactions. Reaction 3 shows a distinct difference in the mass transfer of the silicates relative to Ran 1 or Ran 2 or to the mass transfer determined in Vekol and San Pedro Valleys. Reactions 2 and 3 show that, although Ran 2 and Ran 3 are close together—about 500 ft apart—and the same distance down the flow path, the mass transfer of the silicates is significantly greater at Ran 3 than at Ran 2. The differences in water chemistry between the two wells are shown in figure 24. The differences between the two waters are the result of differences in well depths; Ran 2 is reported to be 870 ft deep and thus does not intercept the evaporites, as does Ran 3, which is 1,005 ft deep. Ran 3 has higher sodium, chloride, and sulfate, and significantly higher calcium, than the shallower well (table 10). Whereas the differences in these four dissolved constituents may be explained by dissolution of halite and gypsum, the differences in the silicate mass transfer cannot.

The poor agreement of the silicates between Ran 2 and 3 may not lie in the difference in the mass transfer of halite and gypsum, or in ion-exchange reactions as determined earlier, but in the mass transfer of total carbon. The ground water is saturated with respect to calcite ( $SI_{cal}=0.192$ ) at Ran 3 but is slightly undersaturated with respect to calcite ( $SI_{cal}=-0.537$ ) at Ran 2 (table 16). The difference in the saturation state of the water may affect the mass transfer of carbon by increasing precipitation of calcite. Reaction 4 shows the mass transfer derived for Ran 3, assuming equal precipitation of calcite for both wells. Values of 3.63 and 0.95 mmol for andesine and augite, respectively, at Ran 3 are in good agreement with 3.83 and 0.93 mmol at Ran 2. The difference between the two wells in total mass transfer for all silicate phases is 0.17 mmol; the small difference in the mass transfer of the individual silicate phases for reactions 2 and 4 may represent the uncertainty of the field and laboratory analytical data. Thus, the difference in chemistry and silicate mass transfer for the two wells may be explained if the differences in bicarbonate concentrations of the two wells are interpreted as additional

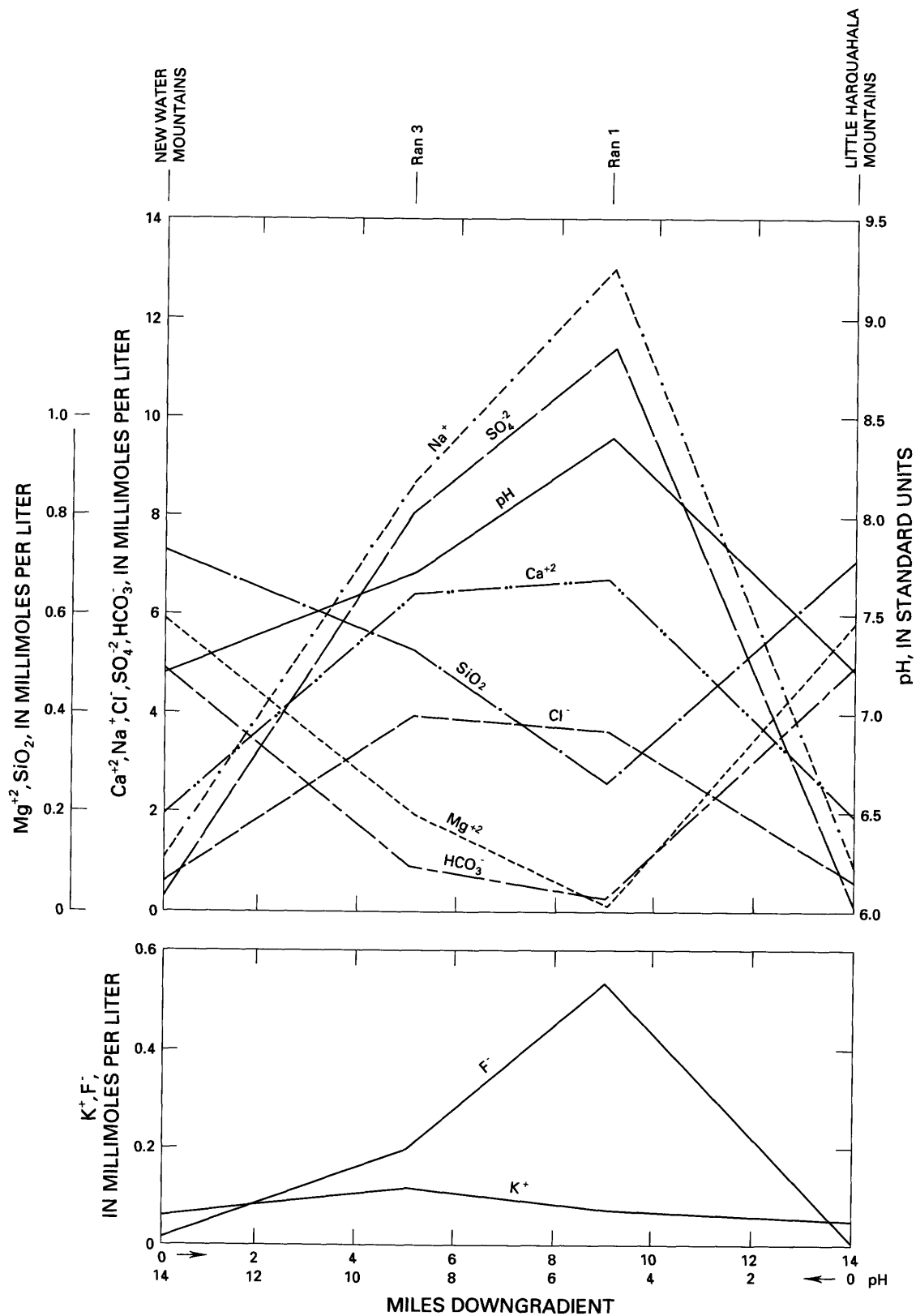


FIGURE 23.—Changes in concentration of dissolved chemical constituents along the flow paths in Ranegras Plain. (Well locations shown in fig. 21.)



TABLE 15.—Summary of mass transfer for Ranegras Plain  
[Values\* in millimoles per kilogram H<sub>2</sub>O; Ran, Ranegras Plain; well names keyed to fig. 21]

Phases	Reaction number and flow path				
	1 Recharge to Ran 1	2 Recharge to Ran 2	3 Recharge to Ran 3	4 Recharge to Ran 3**	5 Vek 3 to Ran 1
O <sub>2</sub> .....	0.15	0.16	0.21	0.17	0.01
CO <sub>2</sub> .....	.60	.55	.57	.57	.00
Calcite .....	-5.05	-3.92	-4.43	-3.92	-1.56
Andesine (An <sub>45</sub> ) .	3.99	3.83	4.28	3.63	.32
Potassium .....	.24	.25	.30	.26	-.08
feldspar					
Augite .....	.86	.93	1.22	.95	.02
Silica .....	-1.61	-1.37	-1.92	-1.55	-.37
Halite .....	3.10	2.82	3.38	3.38	1.47
Gypsum .....	11.24	1.55	7.90	7.90	10.46
Fluorite .....	.26	.13	.09	.09	.25
Montmorillonite..	-3.12	-3.02	-3.39	-2.87	-.19
(mafic)					
Goethite .....	-.29	-.35	-.51	-.38	.00
Ion exchange† ...	3.39	.75	.99	1.18	2.87

\*Reactants are positive and products are negative.

\*\*Calcite precipitation corrected for gypsum.

†Calcium replacing sodium on the substrate.

calcite precipitation caused by the presence of gypsum and larger calcium concentrations in the lower interval.

In addition to the saturation data, the differing pH values and dissolved-oxygen content of the ground water strongly argue against the greater mass transfer. The pH of 7.7 of the water at Ran 3 is significantly lower than the pH of 8.1 at Ran 2 and is anomalously low for a downgradient well. A lower pH would be an expected result of greater calcite precipitation in a closed system. The increase in hydrolysis suggested by reaction 3 would increase the pH of the water at Ran 3, not lower it, and any additional weathering of the silicates would severely deplete the ground water of dissolved oxygen. The oxygen required for weathering of augite per reaction 3 specified by similar reactions shown for Vekol Valley is 7.0 mg/L, a depletion that was not observed at Ran 3, assuming an initial concentration of about 9 mg/L for the recharge waters. Using the mass transfer of augite of 0.95 mmol derived by reaction 4, 5.4 mg/L, or 0.17 mmol, of dissolved oxygen would be removed from solution, which is in accord with measured values. Moreover, as discussed later, the larger increase in ion exchange of calcium replacing sodium is in accord with the larger sulfate concentrations. On the basis of the geology and the overall water chemistry within the basin and other basins, reaction 4, not reaction 3, is more suitable to explain the water chemistry.

The final water composition of Vekol Valley (Vek 3) and the higher salinity water of Ranegras Plain (Ran 1) are compared in figure 25 and illustrate the large differ-

ence in composition. The final waters of both basins are old, greater than 10,000 years, judged by flow distances, hydraulic gradients, and <sup>14</sup>C ages. Reacting the final water composition in Vekol Valley with the final water composition in Ranegras Plain (reaction 5) gives only a slight difference in the mass transfer of the silicates. These differences become even smaller when comparing water from Vek 3 with that from Ran 2 or 3.

The close similarity of the mass transfer of the silicates among the three basins, supported by correspondingly similar saturation states of the ground water, is highly significant and suggests that (1) the geochemical models developed have identified the major reactions that are occurring in the basins and (2) the reactions are indeed transferable among basins. In spite of relatively large differences in the composition of all major dissolved species, the compositions can be related by similar reactions and mass transfer for most phases. The models have defined the nearly identical mass transfer for the silicate phases, the differing mass transfer for gypsum and halite, and an ion exchange of calcium for sodium.

#### McMULLEN VALLEY

McMullen Valley, a long, narrow basin in arid west-central Arizona about 50 mi long and 15 mi wide, is one of the few basins in Arizona bounded chiefly by granitic rocks (fig. 26). The Harcuvar Mountains on the north consist of granite and gneiss, with granite outcropping at the southern and central parts. The Granite Wash Mountains south of the Harcuvar Mountains also consist of granite. The Harquahala Mountains to the south consist chiefly of gneiss, with granite outcroppings in the north-central part. Locally, older metasediments, schist, and volcanic rocks are present (Wilson and others, 1969).

The valley fill has been divided into four units, in ascending order: (1) conglomerate, (2) sand and gravel deposits, (3) playa deposits, and (4) alluvium (Kam, 1964). The conglomerate, a unit of low permeability, has not been encountered extensively by drilling; near Aguila, the unit has been penetrated at 850 ft. The second unit, probably lower basin fill, consists of unsorted clay, sand, and gravel but may contain beds of sorted sand and gravel that yield large amounts of water to wells. The coarse-grained facies of this unit forms the major aquifer of the basin. Overlying the sand and gravel deposits are playa deposits that consist of clay, silt, fine sand, and, locally, gypsum and halite. These fine-grained deposits extend from approximately midway between Wenden and Aguila to the south end of the basin. Near Wenden, the unit reaches its maximum thickness of 1,000 ft and is described as a reddish-orange to pale-red clay-silt unit containing gypsum and halite. The unit decreases in thickness to the southwest. Overlying the

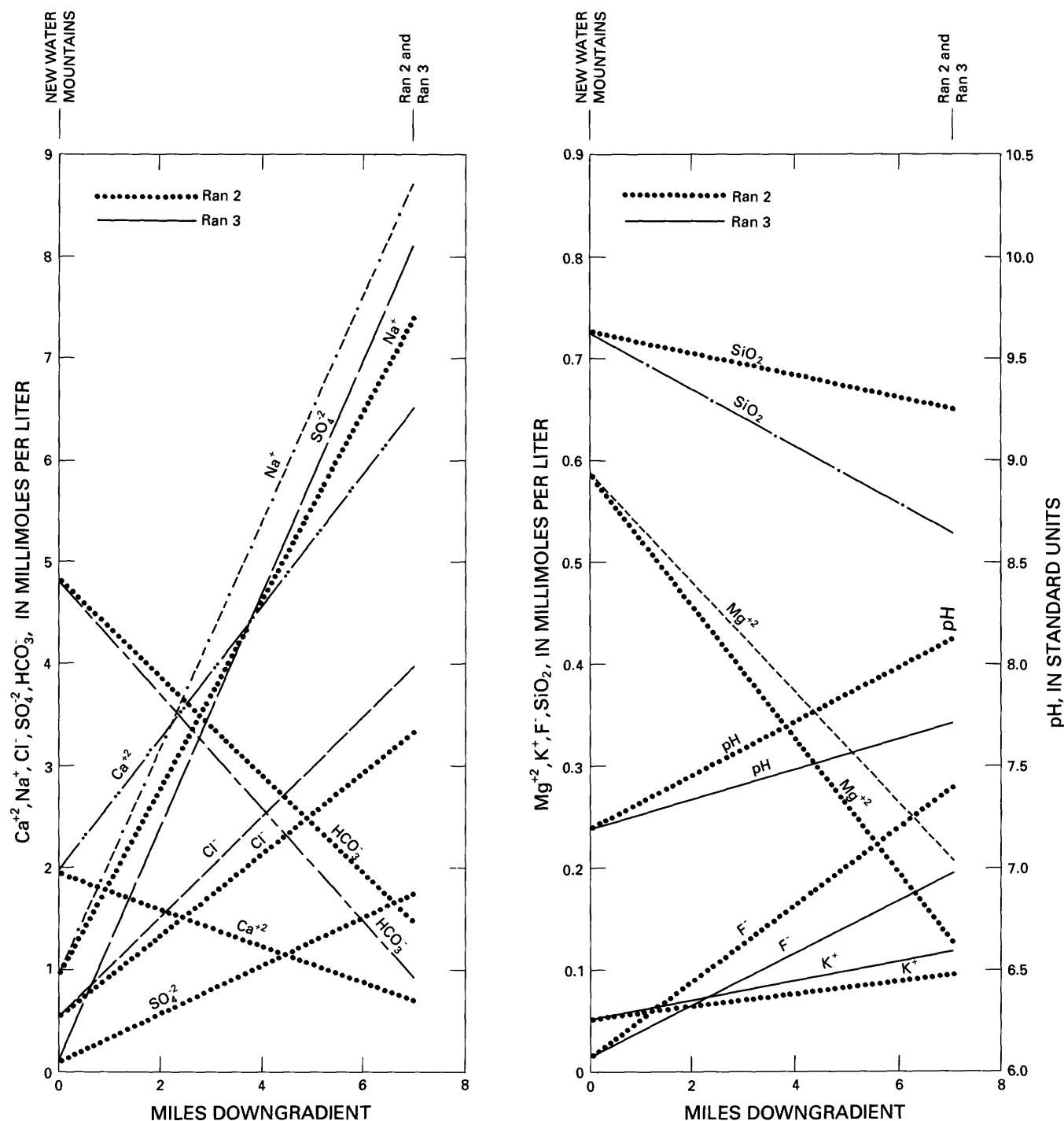


FIGURE 24.—Changes in concentration of dissolved chemical constituents along the flow path to wells Ranegras 2 and Ranegras 3. (Well locations shown in fig. 21.)

playa deposits are clay, sand, and gravel of the alluvium, which for the most part lies above the water table.

Predevelopment depth to the water table at midbasin ranges from about 125 ft near Salome to 425 ft near Wenden. Recharge occurs primarily from runoff from the Harecuvar and Harquahala Mountains. Ground water

occurs chiefly under unconfined conditions (Kam, 1964). The ground water is characterized as a sodium bicarbonate or sodium mixed-anion type (fig. 27). In general, the quality is good and the water is suitable for most purposes; dissolved-solids concentrations generally range between 250 and 500 mg/L. As in many basins in

TABLE 16.—*Saturation indices of the ground water in Ranegras Plain with respect to various minerals*  
 [Ran, Ranegras Plain; well locations shown in fig. 21. Phases and thermodynamic data from Ball and others (1980). Dashes indicate values not calculated]

Phases	Ran 1	Ran 2	Ran 3	Number of samples	Saturation indices for basin		
					Maximum	Minimum	Average
Adularia.....	-0.832	—	-0.107	14	0.582	-1.665	-0.471
Albite.....	-1.010	—	-.735	14	-.111	-2.075	-1.314
Calcite.....	.875	-.537	.192	44	.368	-.537	-.142
Chalcedony.....	-.219	.659	.205	44	.659	-.196	.131
Clinoenstatite.....	-1.665	-4.042	-3.101	43	-1.701	-4.370	-2.890
Diopside.....	1.576	-4.032	-1.997	43	-.448	-4.743	-2.360
Dolomite.....	-.440	-2.161	-1.030	44	.559	-2.160	-.921
Fluorite.....	—	.724	.698	44	1.252	-1.660	.044
Goethite.....	—	—	5.639	—	—	—	—
Gypsum.....	-.149	-1.491	-.235	43	.070	-2.289	-1.507
Halite.....	-6.086	-6.212	-6.204	—	—	—	—
K-mica.....	-2.021	—	-.396	14	1.654	-2.860	-.872
Montmorillonite CA.....	-.793	—	1.401	14	2.869	-.802	.732
Montmorillonite BF.....	—	—	4.845	14	5.249	3.142	4.434
Montmorillonite AB.....	—	—	4.016	14	4.495	2.471	3.633
Tremolite.....	11.143	—	.398	—	—	—	—

the western part of the study area, however, fluoride or chromium locally may present a water-quality problem.

Nine reactions were derived to define the ground-water evolution along two flow paths within the basin (table 17). Six of the reactions define the mass transfer along a flow path in the lower, or southern, part of the valley between the Harcuvar Mountains to McM 1 (McMullen 1) and to McM 2 in the center of the valley near Salome. Three of the reactions define the mass transfer in the upper, or northern, part between the Vulture Mountains to McM 3 and to McM 4 in the center of the valley west of Aguila. The water chemistry of the four wells is summarized in table 10, and the changes in chemistry along the flow paths in the southern and northern parts are shown in figures 28 and 29, respectively.

Multiple reactions were developed because of two possible sources of iron and magnesium (biotite and hornblende) and a suspected range in composition of oligoclase between  $An_{20}$  and  $An_{30}$ . Biotite and hornblende are associated with the calcic granites. Thin-section petrography shows that biotite is the dominant ferromagnesian mineral in the Harcuvar and Harquahala Mountains and that hornblende is dominant in the Granite Wash Mountains. Numerous diorite dikes containing hornblende are present in the Harcuvar and Harquahala Mountains.

In the southern part of the basin, four reactions were modeled using oligoclase  $An_{30}$  and biotite (reactions 1, 2, 3, and 6), one using oligoclase  $An_{25}$  and hornblende (reaction 4), and one using oligoclase  $An_{25}$  and biotite (reaction 5). Using ion-exchange constraints as a guide

for probable reactions, the reactions using  $An_{30}$  and biotite appear suitable with little exchange of calcium for sodium, about 0 to 0.1 mmol of calcium. This value is consistent with the concept of ion exchange not occurring in dilute waters; therefore, reactions 1, 2, 3, 5, and 6 generally are more suitable to explain the water chemistry. Reaction 4 using hornblende shows that ion exchange increases to 0.3 mmol of calcium. On the basis of data presented later, reaction 4 is less favored because the increase in gypsum is less than 0.3 mmol between the initial and final waters and exchange should not occur. A reaction using oligoclase  $An_{30}$  and hornblende (not shown) was modeled but, like reaction 4, was not considered because of 0.41 mmol of calcium replacing sodium. A reaction using oligoclase  $An_{20}$  and biotite, a common assemblage for granite (not shown), was considered but was not realistic because of an improbable exchange of sodium replacing 0.56 mmol of calcium. Reactions 4 and 5 indicate that the granitic rocks are slightly more calcic than true plutonic alkali granites. These ion-exchange constraints are admittedly somewhat arbitrary, particularly in view of the uncertainty of the compositions and presence of the minerals involved. However, reactions 1, 2, 3, 5, and 6 are consistent with the observed geology and with the hypothesis regarding ion exchange developed throughout this report.

The mass transfer of hornblende and biotite for all reactions to McM 2 is between 0.39 and 0.47 mmol, with apparently little weathering of these minerals downgradient between McM 1 and McM 2. Like augite, the weathering of biotite and hornblende appears to be related to the regional flow system. For the oxidation of

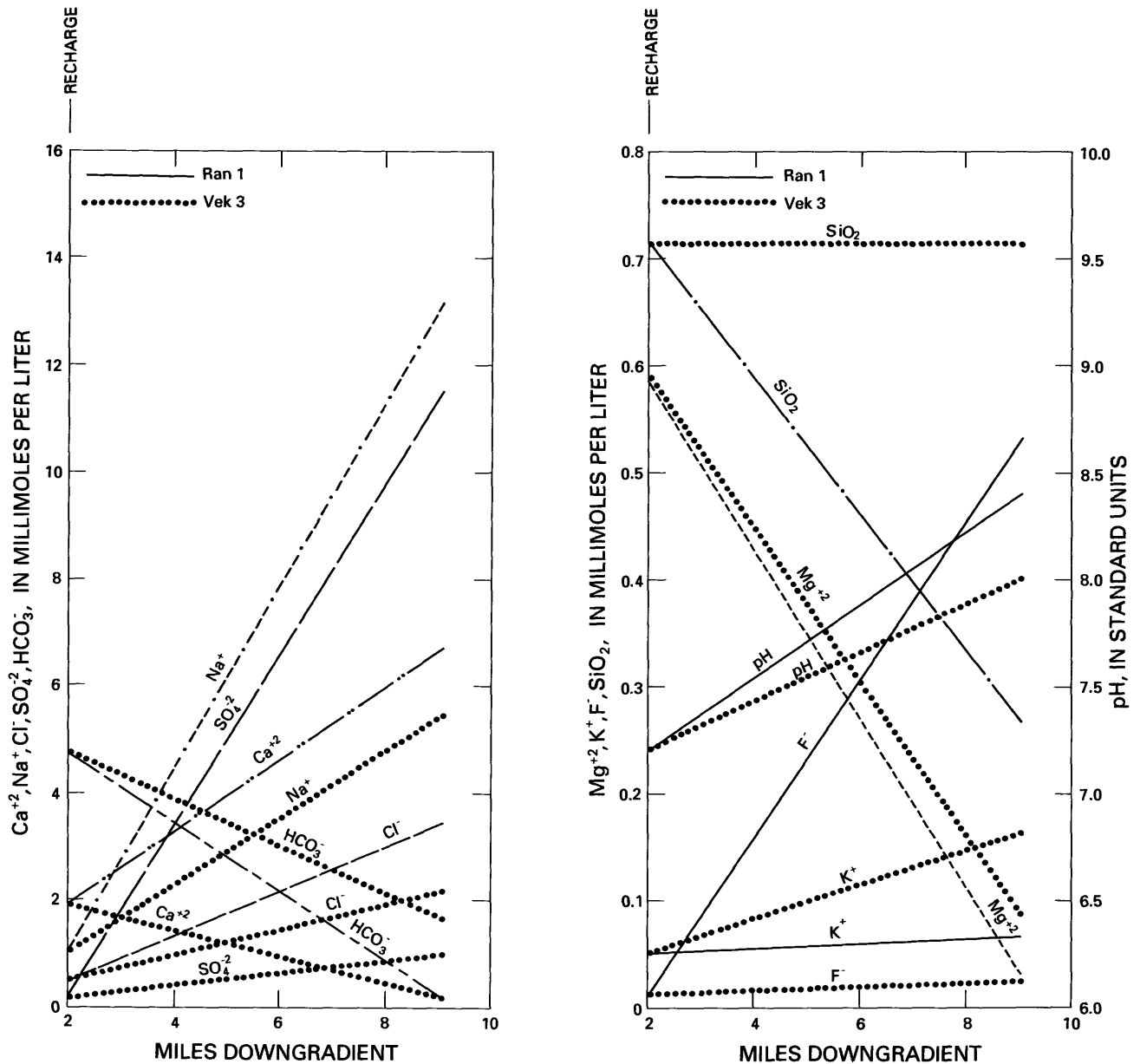
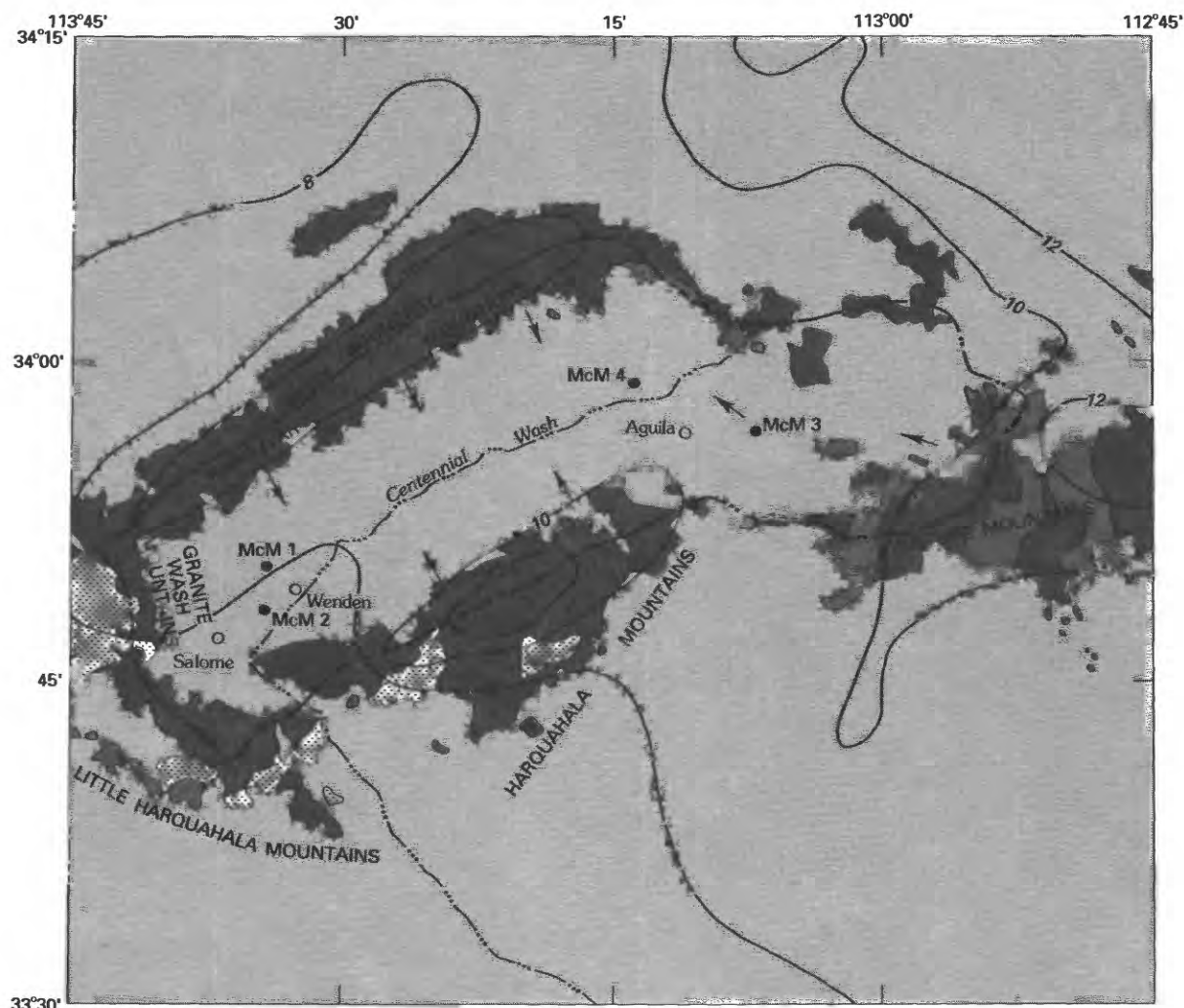


FIGURE 25.—Comparison of ground-water compositions in Vekol Valley and Ranegras Plain. (Well locations shown in figs. 15, 21.)

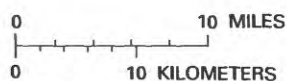
iron in 0.46 mmol of biotite, 0.17 mmol, or 5.5 mg/L, of oxygen is consumed, which would be in good agreement with measured values from the southern part of the valley. The total mass transfer of the oligoclase ranges from 3.29 to 4.13 mmol depending on the source mineral(s) for calcium. The total mass transfer of oligoclase An<sub>30</sub> ranges between 3.93 and 3.97 mmol. For comparison purposes, reaction 6 shows the mass transfer from recharge to McM 2 with potassium included in biotite. With the exception of decreasing slightly the already small mass transfer of potassium feldspar, the other phases are not greatly affected, for example, the

small difference in the mass transfer cited for oligoclase An<sub>30</sub>.

Some differences in chemistries are seen between the ground water in McMullen Valley and that in Vekol Valley and Ranegras Plain. The concentrations of bicarbonate, calcium, and magnesium, which are typical of other wells sampled in the lower part of the valley, appear to decrease less downgradient than those in mafic basins, assuming identical composition of the recharge waters for both basin types. In accordance with the differences in chemistries, smaller mass transfer of the silicate minerals is derived for the felsic basin than for



Base from U.S. Geological Survey  
State base map, 1974, 1:500,000



## EXPLANATION








-  ALLUVIUM
-  INTERMEDIATE VOLCANIC ROCKS
-  SEDIMENTARY ROCKS
-  GRANITIC AND METAMORPHIC ROCKS
-  —10— LINE OF EQUAL AVERAGE ANNUAL PRECIPITATION,  
1930-60—Interval, in inches, is variable
-  → DIRECTION OF GROUND-WATER MOVEMENT
-  ● McM 1 WELL—McM 1 is well identifier

FIGURE 26. —Generalized geology, wells, and ground-water movement in McMullen Valley.

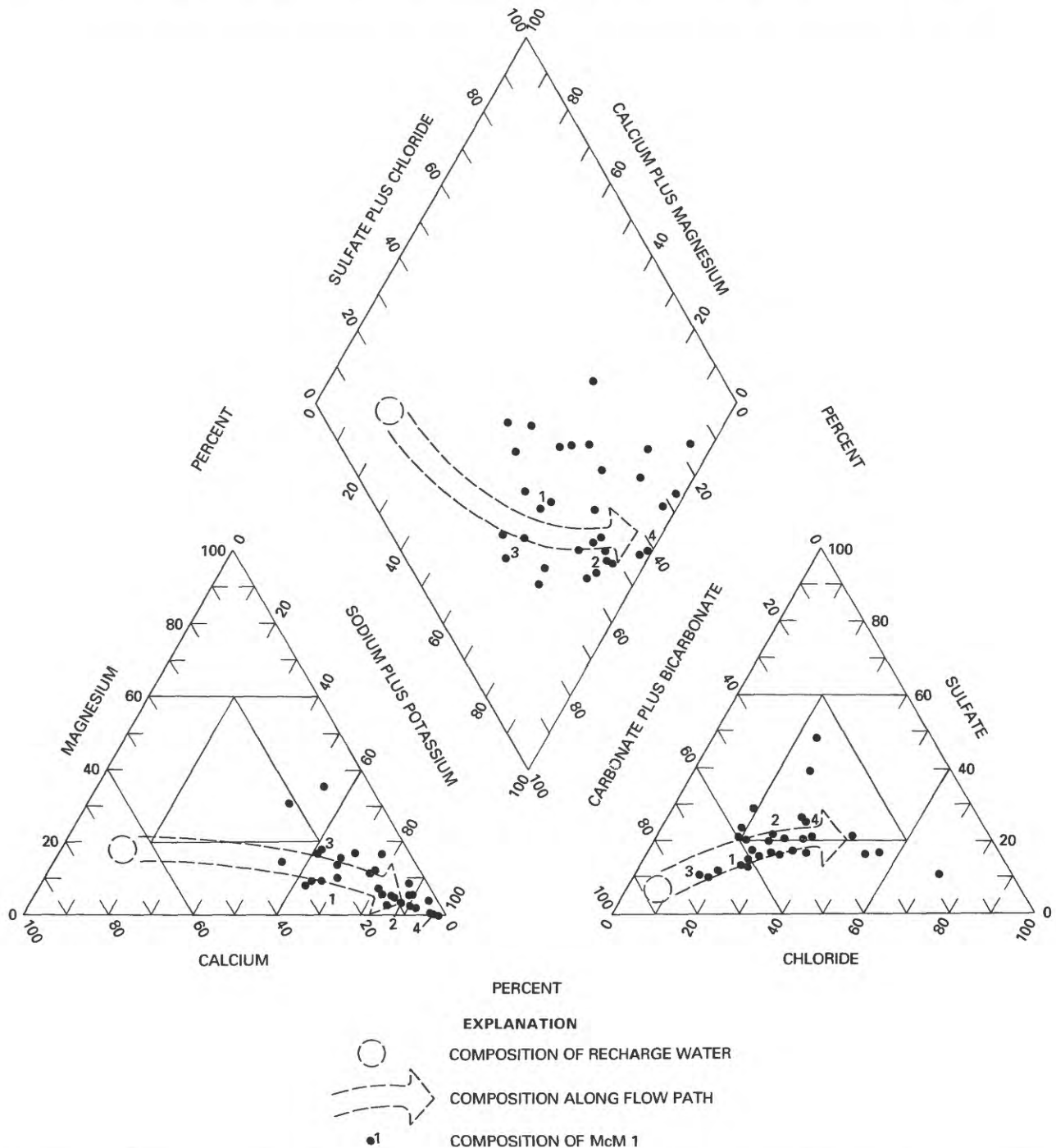


FIGURE 27.—Relative compositions of ground water in McMullen Valley, in equivalent percents. (Well locations shown in fig. 26.)

the mafic basins. Total silicate mass transfer of about 4.1 to 5.0 mmol for McMullen Valley is compared with 4.9 to 5.8 mmol for the mafic basins. The difference may be due to the weathering rates of the lower temperature minerals.

On the basis of minerals selected and initial and final water compositions, about 4 mmol of oligoclase  $An_{25}$  to  $An_{30}$  and about 0.5 mmol of biotite with minor horn-

blende are weathered. The derived phases and weathering sequences agree with the subsurface geology of the area and, except for the Aberdeen and Belle Fourche montmorillonites, with the saturation state of the ground water (table 18). The lithologic log of well (B-6-12)15bbb near Wenden reveals that the coarse-grained facies underlying the reddish playa deposits consist of granite, gneiss, schist, and quartz fragments (Kam, 1964).

TABLE 17.—Summary of mass transfer for McMullen Valley

[Values\* in millimoles per kilogram H<sub>2</sub>O; McM, McMullen Valley; well names keyed to fig. 26. Dashes indicate phase not used]

Phases	Reaction number and flow path**								
	1 Recharge to McM 1	2 McM 1 to McM 2	3 Recharge to McM 2	4 Recharge to McM 2	5 Recharge to McM 2	6 Recharge to McM 2	7 Recharge to McM 3	8 Recharge to McM 3	9 Recharge to McM 4
O <sub>2</sub> .....	0.18	0.00	0.17	0.12	0.17	0.15	0.18	0.12	0.17
CO <sub>2</sub> .....	.51	.06	.57	.57	.57	.57	.57	.57	.60
Calcite .....	-2.27	-.62	-2.89	-2.89	-2.89	-2.89	-2.98	-2.98	-3.76
Oligoclase (An <sub>25</sub> ) .....	—	—	—	3.29	4.13	—	—	—	—
Oligoclase (An <sub>30</sub> ) .....	3.03	.94	3.97	—	—	3.93	3.48	—	—
Andesine (An <sub>45</sub> ) .....	—	—	—	—	—	—	—	2.77	4.24
Potassium feldspar .....	.34	.05	.39	.31	.39	.04	.37	.17	.19
Augite .....	—	—	—	—	—	—	—	.66	.90
Hornblende .....	—	—	—	.47	—	—	—	—	—
Biotite .....	.44	.02	.46	—	.46	†.39	.49	—	—
Silica .....	-2.19	-.42	-2.61	-3.02	-3.25	-2.02	-2.42	-1.22	-1.46
Halite .....	.62	.14	.76	.76	.76	.76	.00	.00	.82
Gypsum .....	.25	.07	.32	.32	.32	.32	.01	.01	.25
Fluorite .....	.03	.02	.05	.05	.05	.05	.12	.12	.09
Montmorillonite (felsic) .....	-2.37	-.65	-3.02	-2.46	-3.02	-2.74	-2.70	—	—
Montmorillonite (mafic) .....	—	—	—	—	—	—	—	-2.17	-3.27
Goethite .....	-.42	.03	-.39	-.22	-.39	-.31	-.47	-.24	-.30
Ion exchange†† .....	.05	.08	.13	.30	-.02	.15	-.46	.00	.33

\*Reactants are positive and products are negative.

\*\*Reactions 1 through 6 refer to lower basin, 7 through 9 to upper basin.

†Potassium included in biotite.

††Calcium replacing sodium on the substrate.

In modeling reactions in the upper part of the basin, phases used in the lower part were considered probable phases on an assumed homogeneous geology of the Harquahala and Harcuvar Mountains throughout the basin. Reaction 7, which defines the mass transfer along the flow path from recharge areas to McM 3 using oligoclase An<sub>30</sub> and biotite, is considered unlikely, however, because of an unrealistically large exchange of 0.92 mmol of sodium for calcium. A reaction with substitution of hornblende for biotite (not shown) also gives an exchange of 0.42 mmol of sodium for calcium. Reactions 8 and 9, using andesine An<sub>45</sub> and augite, define mass transfer that is consistent with the water chemistry and with that determined in other basins. Compatible mass transfer is derived by compensating for solute calcium through higher calcic phases of the mafic model.

The surficial geology appears similar in upbasin and downbasin areas; however, examination of geologic logs from the upper part show that the subsurface geology in the west half of T. 7 N., R. 8 E., contains abundant basalt flows and fragments. Basalt flows are confirmed from 340 to 1,704 ft below the land surface. The geologic log of Department of Energy test well (B-8-9)29dc just north of the flow path between the Harcuvar Mountains and McM 4 also shows abundant basalt between the land surface and 740 ft and traces of basalt between 740 and 3,910 ft

below the land surface (U.S. Geological Survey, unpub. data). Using the reactant and product phases of the mafic model, the mass transfer determined is consistent with the observed subsurface geology and, although not so obviously, with the surficial geology. The higher ion-exchange value derived by reaction 9 suggests that McM 4 may be located in a transitional zone between the mafic and felsic terranes.

Reaction 9 also shows that, unlike the trend in other basins, the ferromagnesian mineral (augite) is weathered downgradient. Assuming the changes in chemistry do indeed represent changes along the true flow path, the weathering of additional augite and andesine may be explained through the presence of unweathered basalt within the alluvium, as high-temperature ferromagnesian minerals are not stable in the low-temperature weathering environment. (The question of the flow path is raised because, of all the paths modeled, the flow path to McM 4 is the least defined; some underflow may be recharged near the northernmost parts of the Harcuvar Mountains.) The pH of 9.4 of the ground water at McM 4 is indicative of the extent of the hydrolysis reactions. This pH measurement was the highest in the entire study area. The derived mass transfer of the silicates predicts a highly alkaline solution, which is in agreement with this observed high pH value.



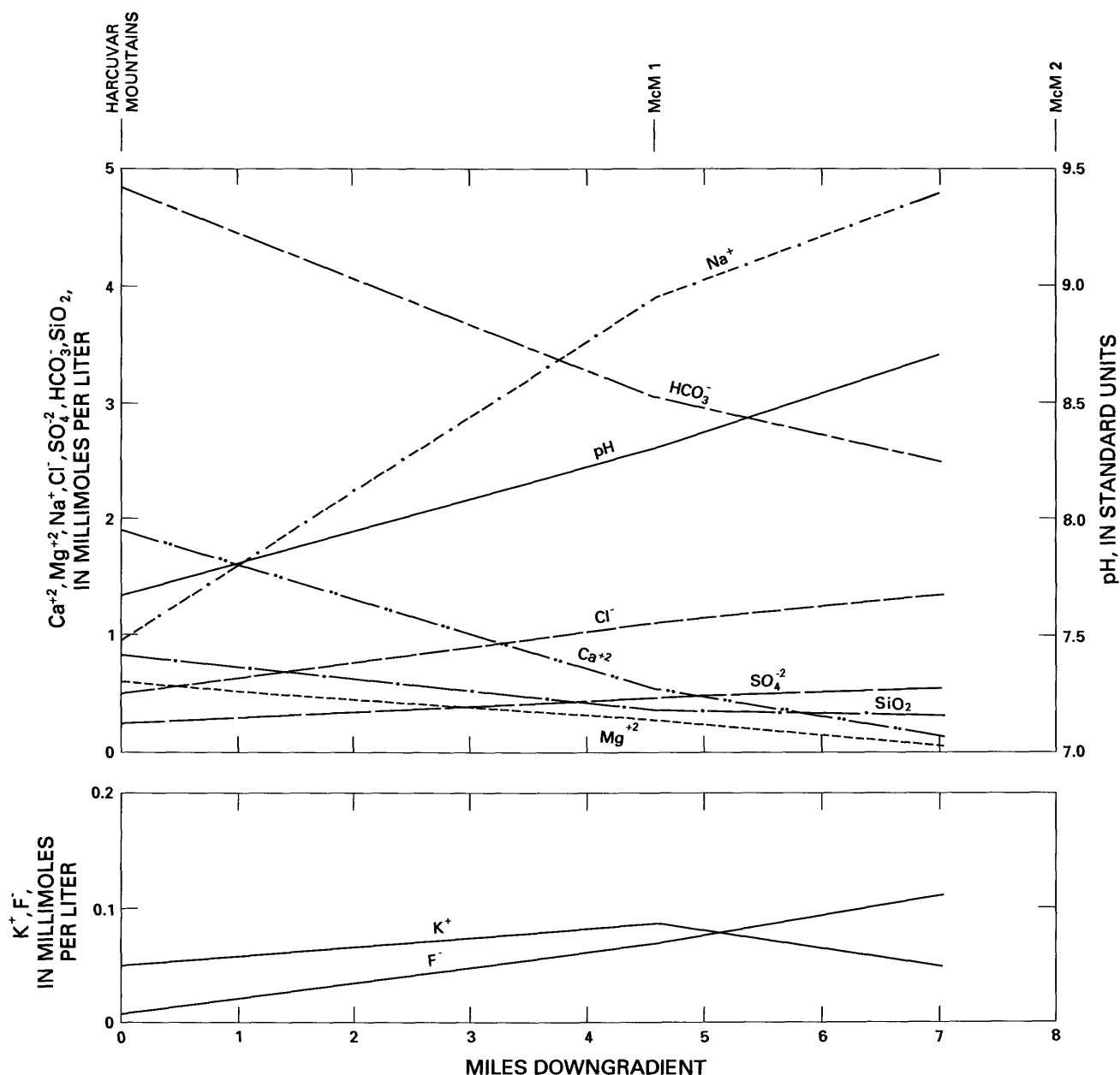


FIGURE 28.—Changes in concentration of dissolved chemical constituents along the flow path in lower McMullen Valley. (Well locations shown in fig. 26.)

#### WILLCOX BASIN

The Willcox basin is typical of several large, broad basins in semiarid southeastern Arizona. These broad basins contrast with narrow basins like the San Pedro Valley. The Willcox basin is the highest in altitude of the basin lowlands, about 4,100 ft above sea level, and is surrounded by mountains with altitudes greater than 10,000 ft. The mountains that bound the basin receive relatively high precipitation; for example, annual precipitation in the Chiricahua Mountains exceeds 35 in. The Willcox basin is the only topographically closed basin in

the study area with centripetal drainage that discharges ground water toward its center at the Willcox Playa (fig. 30). The basin also is unique geochemically and hydrologically among those modeled because a major portion of the recharge apparently is a result of infiltration of precipitation and runoff along the valley floor throughout much of the basin.

The Chiricahua and the Dos Cabezas Mountains bound the basin on the east, the Dragoon and Winchester Mountains on the west, and the Pinaleno Mountains on the north. The Chiricahua and Winchester Mountains are

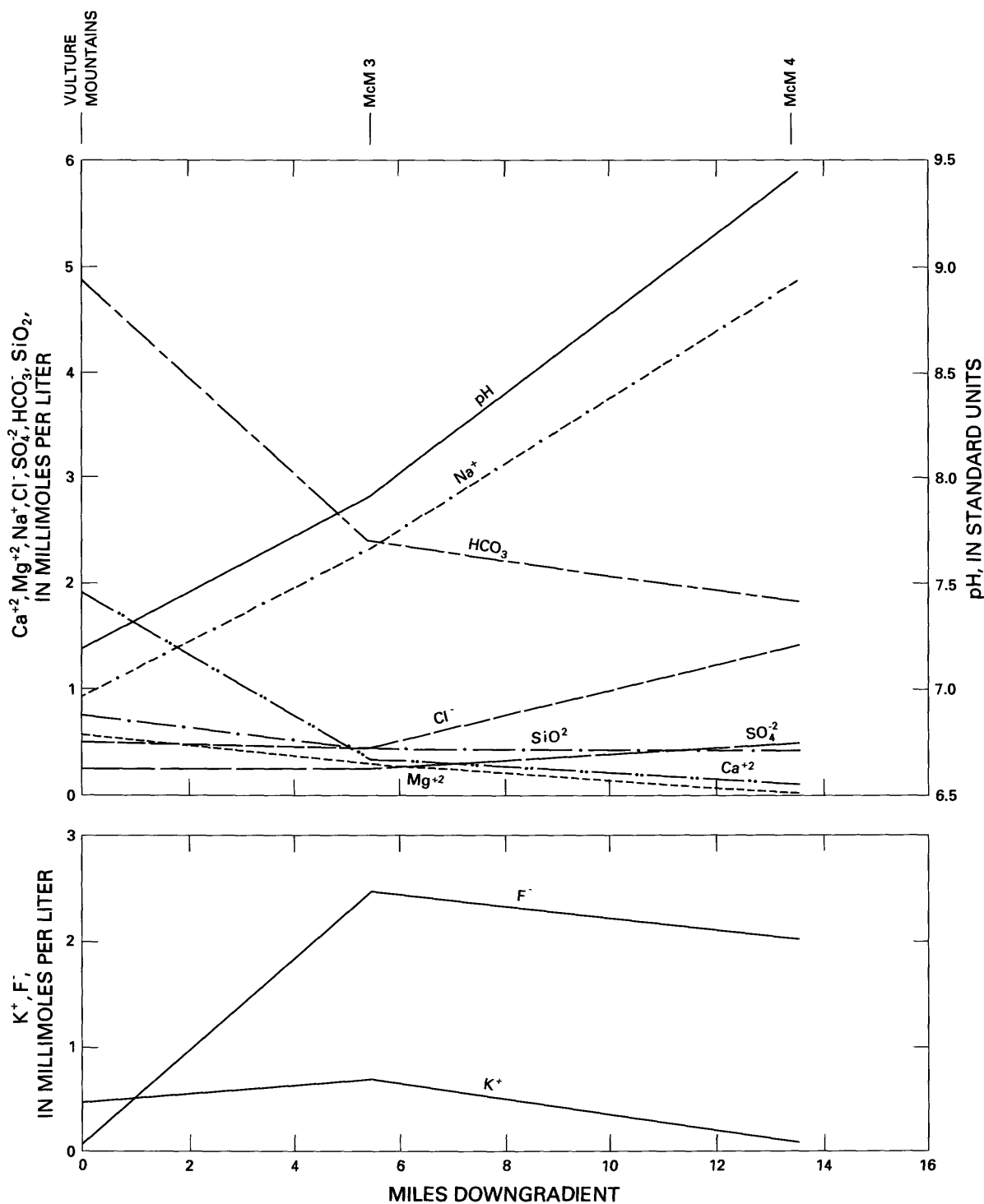


FIGURE 29.—Changes in concentration of dissolved chemical constituents along the flow path in upper McMullen Valley. (Well locations shown in fig. 26.)

predominantly silicic volcanic rocks, and the Dos Cabezas and Dragoon Mountains are predominantly granitic and volcanic rocks. The Pinaleno Mountains consist chiefly of granite and granitic gneiss. The basin fill consists of alluvial and stream deposits that contain clay, silt, sand,

gravel, cobbles, and boulders. The permeable stream deposits of the upper basin fill, which range from a few hundred feet to more than 1,000 ft thick, constitute the most important aquifer of the Willcox basin (Brown and Schumann, 1969). The confining clayey layer overlying

TABLE 18.—*Saturation indices of the ground water in McMullen Valley with respect to various minerals*

[McM, McMullen Valley; well locations shown in fig. 26. Phases and thermodynamic data from Ball and others (1980)]

Phases	McM 1	McM 2	McM 3	McM 4
Adularia.....	-1.130	-1.422	-1.395	-1.022
Albite.....	-1.937	-1.905	-2.366	-.920
Calcite.....	.079	-.134	-.174	-.178
Chalcedony.....	.032	-.011	.064	-.063
Clinoenstatite.....	-2.456	-2.421	-2.452	-3.198
Diopside.....	-1.994	-1.773	-2.090	-1.452
Dolomite.....	-.025	-.572	-.385	-2.572
Fluorite.....	-.919	-1.021	-.012	-1.273
Goethite.....	5.827	6.043	6.051	5.179
Gypsum.....	-2.100	-2.498	2.851	-3.296
Halite.....	-7.020	-6.866	-7.696	-6.851
K-mica.....	-2.468	-3.376	-3.670	-2.571
Montmorillonite CA....	-.545	-1.378	-1.297	-.916
Montmorillonite BF....	3.736	3.171	2.921	3.451
Montmorillonite AB....	3.058	2.616	2.357	2.644
Tremolite.....	1.945	2.559	1.961	.682

the aquifer in other basins is not present in the Willcox basin.

Depths to water are considerably shallower relative to most basins and range from about 200 to 400 ft at the mountain front, in the case of the Chiricahua Mountains, to less than 20 ft as the playa is approached. The major recharge area of the basin is adjacent to the Chiricahua Mountains that bound the southeastern part of the basin. Estimated annual recharge to the basin is 54,000 to 75,000 acre-ft. Nearly one-half of this amount originates near the Chiricahua Mountains and flows through the Kansas Settlement area; some recharge originates near the Dos Cabezas Mountains (Brown and Schumann, 1969). Recharge from the Pinaleno Mountains, which also receive annual precipitation in excess of 35 in, drains partly into Aravaipa Valley to the north as well as into the Willcox basin. The waters are low in dissolved solids throughout much of the basin. Chloride and sulfate concentrations commonly are less than 10 mg/L. The ground water is a calcium sodium bicarbonate or sodium calcium bicarbonate type.

Reactions were modeled along a flow path of about 30 mi, from the origin of Turkey Creek, the major drainage area of the Chiricahua Mountains, along the area near Turkey Creek to the playa (fig. 30). Oligoclase  $An_{25}$  and biotite were selected as the probable silicate reactant phases on the basis of the geology of the Chiricahua Mountains. The granitic and syenitic gneisses and the extensively developed acidic lavas found in the Dos Cabezas and Chiricahua Mountains contain chiefly quartz, feldspar, and mica (Meinzer and Kelton, 1913).

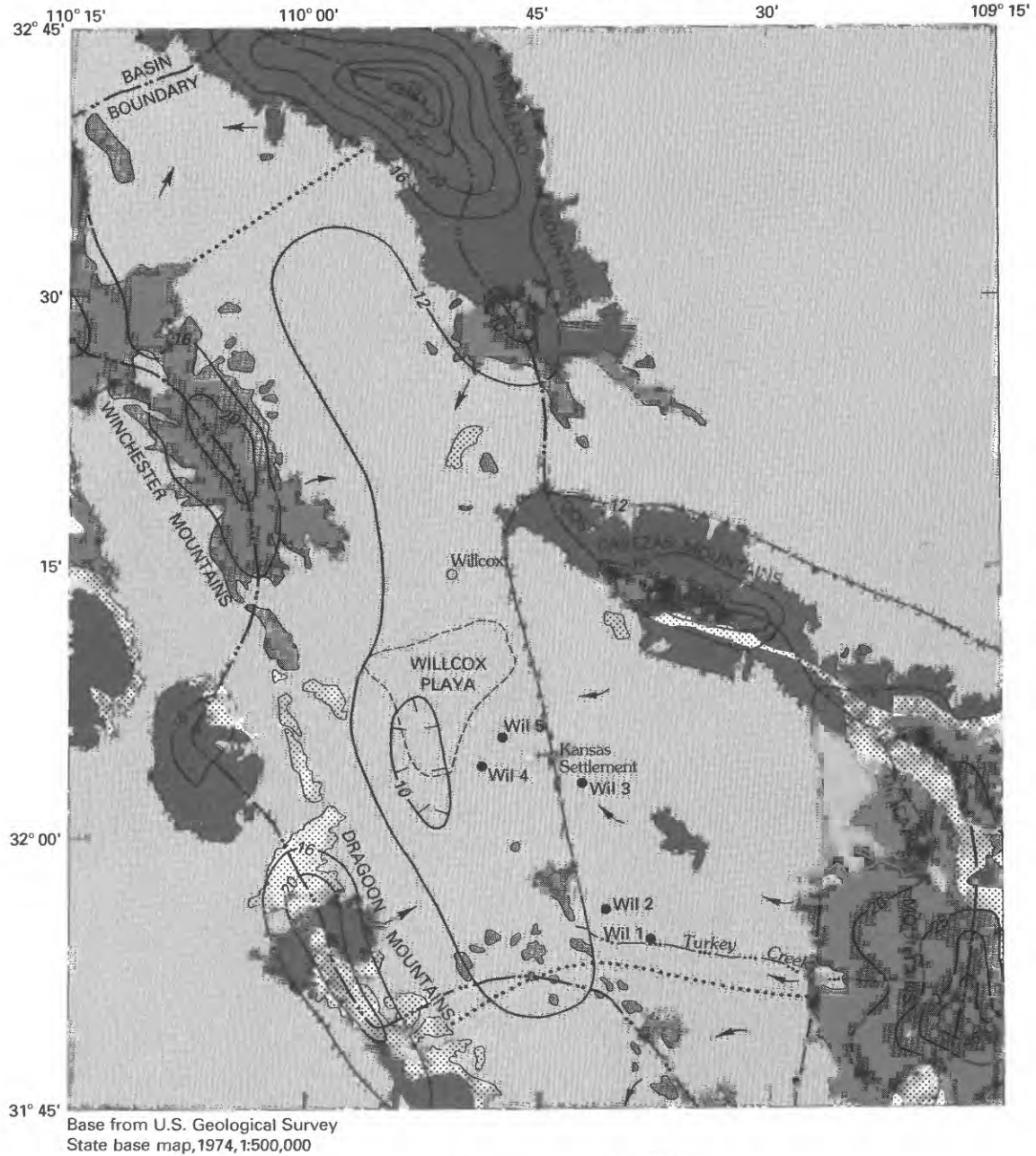
In contrast to the definite water-chemistry patterns observed along the flow path of dilute waters in other basins, trends in the Willcox basin are less clear (fig. 31). Bicarbonate, calcium, and silica increase and sodium,

sulfate, chloride, and pH decrease at points along the flow path. The difference in water chemistry is accompanied by differing mass transfer that is inconsistent with that of other basins or is not thermodynamically valid.

Reaction 1 in table 19 shows the mass transfer derived from recharge to Wil 1 (Willcox 1) using biotite and oligoclase. The reaction is thermodynamically valid but shows an improbable ion exchange of 2.32 mmol of sodium replacing calcium. Reaction 2 derives the mass transfer to Wil 1 using minerals with larger calcium content to affect lower solute sodium. The exchange of sodium for calcium is reduced only slightly; thus reaction 2 or other reactions with reactants higher in calcium would not be valid in terms of the mass balance of sodium and calcium. Reaction 3, showing the mass transfer from recharge to Wil 2, is nearly identical to reaction 1. For subsequent reactions, reactions 4, 5, and 6 between Wil 2 and the playa, phases are derived that do not agree with the speciation data and the saturation state of the ground water (table 20). The mass transfer of the silicate phases is reversed; potassium feldspar, plagioclase, and biotite are precipitating out of solution and montmorillonite, goethite, and silica are dissolving.

The difference between the mass transfer determined for the Willcox basin and for basins previously discussed may be explained by the mixing of additional recharge water with underflow owing to the shallow water table and permeable deposits. In the basins previously discussed, a geochemically closed system was postulated and was subsequently supported by the mass-transfer calculations, the aqueous speciation and saturation data, and, in most basins, the isotope data. Depths to water in these basins generally ranged from 125 to 500 ft in the shallow parts to more than 800 ft near the mountains. Predevelopment depth to water was about 120 ft at Wil 1 and about 80 ft at Wil 2 (Meinzer and Kelton, 1913). The overlying coarse-grained deposits and relatively large amounts of precipitation and runoff apparently allow significant recharge through the overlying deposits to depths as great as 120 ft. As depths to water decrease downgradient, leakage and mixing increase, which results in the reversed trends in chemistry and mass transfer.

Recharge through the overlying sediments throughout the basin can be interpreted from trends in the trilinear diagram (fig. 32) and from the isotope data. The trilinear diagram indicates that calcium, magnesium, and bicarbonate ions are predominant or occur in relatively larger concentrations than in similar dilute waters of Vekol, San Pedro, or McMullen Valleys. The ground water throughout the Willcox basin is generally characterized by high calcium, magnesium, and bicarbonate—typical of recharge waters—and does not evolve into a sodium



0 10 MILES  
0 10 KILOMETERS

## EXPLANATION

- |  |                                |  |   |
|--|--------------------------------|--|---|
|  | ALLUVIUM                       |  | 20 — LINE OF EQUAL AVERAGE ANNUAL PRECIPITATION, 1930-60—Interval, in inches, is variable |
|  | SILICIC VOLCANIC ROCKS         |  | DIRECTION OF GROUND-WATER MOVEMENT  |
|  | SEDIMENTARY ROCKS              |  | WELL—Wil 1 is well identifier   |
|  | GRANITIC AND METAMORPHIC ROCKS |  | GROUND-WATER DIVIDE   |

FIGURE 30.—Generalized geology, wells, and ground-water movement in the Willcox basin.

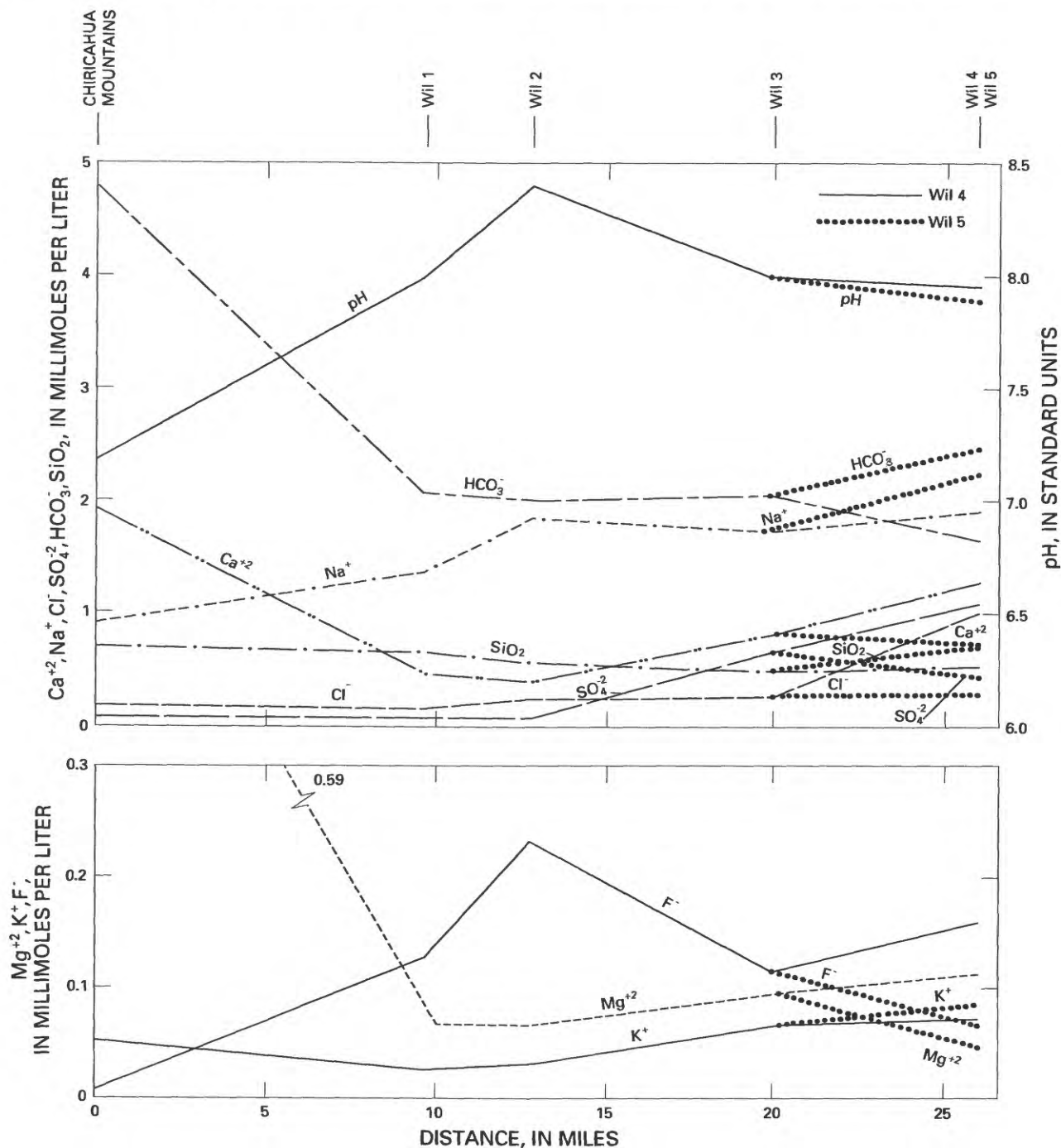


FIGURE 31.—Changes in concentration of dissolved chemical constituents along the flow path in the Willcox basin. (Well locations shown in fig. 30.)

mixed-anion or sodium chloride sulfate water, as does water in basins that evolve under closed conditions. Isotope data also lend some support to an open system. Wil 4, one of the two farthest downgradient wells, is in a sandy area that has no significant irrigation history onsite or upgradient for several miles. The well was recently deepened from 350 to 500 ft, and most of the

800-gal/min yield is contributed from a 400- to 500-ft sandy zone. Depth to water, which is near predevelopment levels, is 50 ft. A <sup>14</sup>C measurement of the tritium-free water (<0.2 TU) was 26 PMC, which is unusually high. Unless a process such as gaseous diffusion (Thorstenson and others, 1983) or exceptionally high ground-water velocities are considered, the <sup>14</sup>C activity

TABLE 19.—*Summary of mass transfer for the Willcox basin*[Values\* in millimoles per kilogram H<sub>2</sub>O; Wil, Willcox basin; well names keyed to fig. 30. Dashes indicate phase not used]

Phases	Reaction number and flow path					
	1 Recharge to Wil 1	2 Recharge to Wil 1	3 Recharge to Wil 2	4 Wil 2 to Wil 3	5 Wil 2 to Wil 4	6 Wil 2 to Wil 5
O <sub>2</sub> .....	0.18	0.11	0.18	—	—	—
CO <sub>2</sub> .....	.56	.56	.58	-0.02	-0.02	-0.06
Calcite .....	-3.31	-3.31	-3.39	.05	-.37	.55
Oligoclase (An <sub>25</sub> ) .....	4.21	—	4.37	-.25	-.13	-.78
Oligoclase (An <sub>30</sub> ) .....	—	3.32	—	—	—	—
Potassium feldspar .....	.37	.15	.39	.02	.03	-.02
Augite .....	—	.63	—	—	—	—
Biotite .....	.47	—	.50	-.02	-.01	-.17
Silica .....	-2.97	-.84	-3.19	.02	-.04	.67
Halite .....	.00	.00	.00	.06	.79	.23
Gypsum .....	.00	.00	.00	.50	1.01	.36
Fluorite .....	.06	.06	.11	-.06	-.04	-.08
Montmorillonite (felsic) ...	-3.07	-2.56	-3.19	.16	.07	.58
Goethite .....	-.41	-.19	-.43	.02	.02	.19
Ion exchange** .....	-1.16	-.49	-1.02	.00	-.30	.35

\*Reactants are positive and products are negative.

\*\*Calcium replacing sodium on the substrate.

shows additional recharge along the 30-mi flow path between the mountain front and Wil 4.

In addition to leakage, another factor to be considered in the Willcox basin is the uncertainty of the composition of the recharge water. Chemical analyses of the ground water near the Chiricahua Mountains are not available to define the possible silicic-sodic composition expected from the weathering of a felsic terrane. The composition of the ground water throughout the eastern part of the basin, however, does not reflect dissolution of a rhyolitic

tuff or weathering of silicic volcanic rocks present in the Chiricahua Mountains; silica and sodium concentrations are smaller, and calcium and magnesium larger, than expected and are consistent with other basins in the study area. In any event, increasing the sodium content of the recharge water, as would be expected with silicic reactions, would not improve the modeling results because the average recharge water already appears too high in sodium. The ground-water compositions in the Willcox basin suggest that reactions involving an open

TABLE 20.—*Saturation indices of the ground water in the Willcox basin with respect to various minerals*

[Wil, Willcox basin; well locations shown in fig. 30. Phases and thermodynamic data from Ball and others (1980). Dashes indicate values not calculated]

Phases	Wil 1	Wil 2	Wil 3	Wil 4	Wil 5	Saturation indices for basin			
						Number of samples	Maximum	Minimum	Average
Adularia .....	—	—	—	—	—	9	0.942	-0.802	0.200
Albite .....	—	—	—	—	—	9	-.036	-1.643	-1.063
Calcite .....	-0.106	0.198	0.151	0.122	0.020	19	0.231	-1.565	-.029
Chalcedony .....	.377	.299	.192	.261	.326	19	.571	.089	.285
Clinoenstatite .....	-2.911	-2.254	-2.883	-3.023	-3.308	19	-2.090	-4.495	-2.929
Diopside .....	-2.215	-.905	-2.030	-2.127	-2.692	19	-.462	-5.637	-2.268
Dolomite .....	-.947	-.336	-.588	-.807	-1.062	19	-.034	-3.587	-.788
Fluorite .....	-.354	.100	-.240	.172	-.722	19	.172	-2.640	-.988
Goethite .....	5.472	5.338	5.858	6.328	5.907	—	—	—	—
Gypsum .....	-3.215	-2.705	-1.769	-1.460	-1.925	19	-1.192	-4.385	-2.574
Halite .....	-8.309	-8.010	-7.961	-7.354	-7.652	—	—	—	—
K-mica .....	—	—	—	—	—	9	1.536	-1.882	-.256
Montmorillonite CA .....	—	—	—	—	—	9	3.197	.272	1.652
Montmorillonite BF .....	—	—	—	—	—	9	4.803	3.275	4.163
Montmorillonite AB .....	—	—	—	—	—	9	4.078	2.726	3.474
Tremolite .....	1.104	5.616	1.228	-.802	-1.351	—	—	—	—

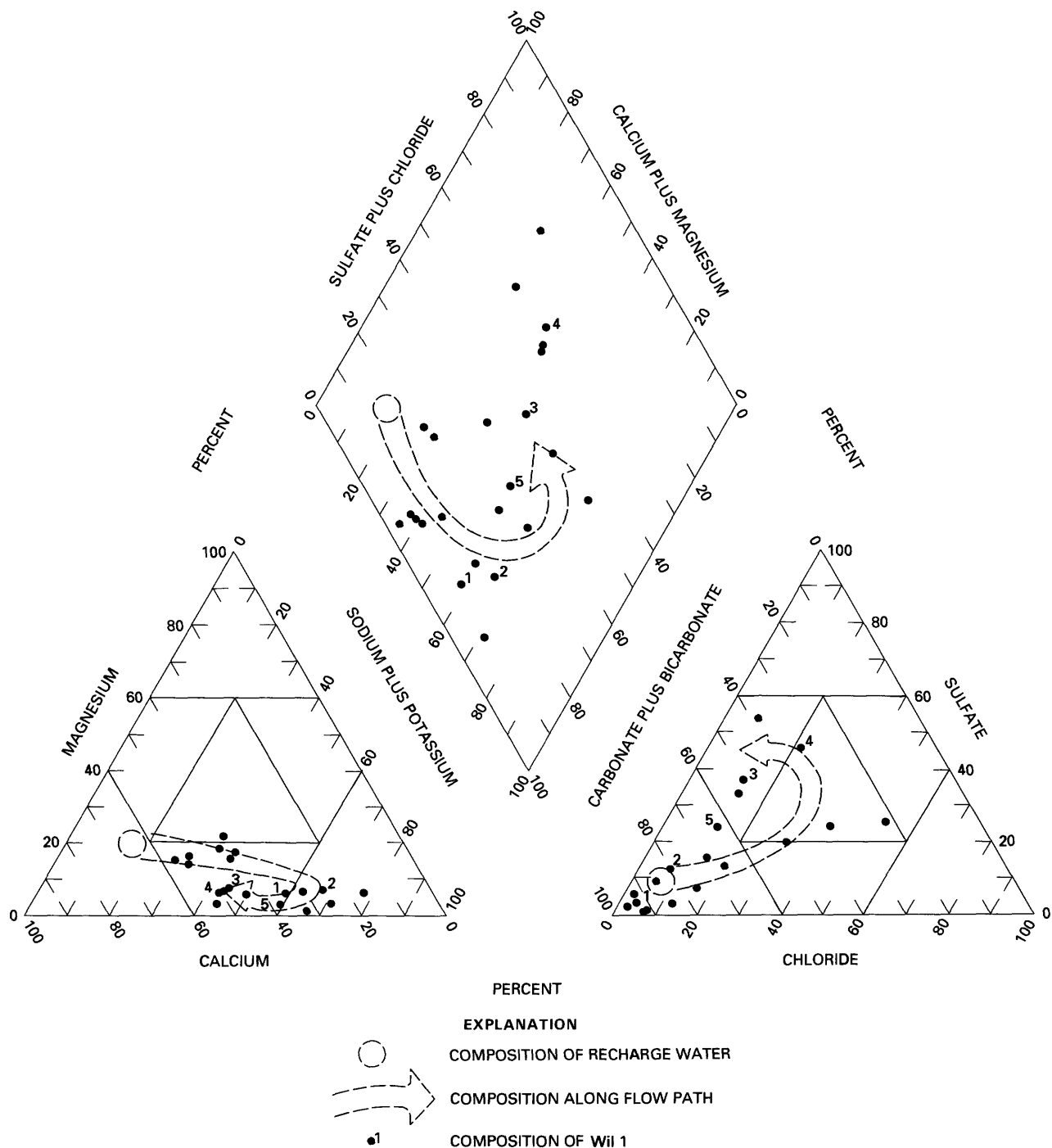


FIGURE 32.—Relative compositions of ground water in the Willcox basin, in equivalent percents. (Well locations shown in fig. 30.)

system or reactions in the unsaturated zone may be as influential as the mineralogy of the surrounding mountains in determining solute chemistry.

Although the mass transfer along the flow path has not been defined, several distinct trends are observed. The system is apparently open to  $\text{CO}_2$ , as observed by a slight decrease in pH downgradient. The ground water downgradient is dissolving carbonate minerals and shows

increases in silica, calcium, and magnesium, all of which are indicative of open-system reactions. The final water compositions near the playa at Wil 4 and Wil 5 show an inverse relation between calcium and bicarbonate. Wil 5 shows larger bicarbonate and smaller calcium concentrations, a result of equilibrium with respect to calcite, which is maintained along the entire flow path. Wil 4 is shallower, and the larger concentrations of calcium are a



result of continuous input of additional calcium through percolating waters and dissolution reactions along the valley floor. In a geochemically closed system, calcium and bicarbonate ions are effectively removed by secondary minerals. The reactions and mass transfer determined for the chemically closed basins and the reactions described above show the importance of open versus closed systems in determining the evolution of the ground-water chemistry.

#### BASINS ALONG THE COLORADO RIVER

The basins along the Colorado River in Arizona, California, and Nevada are unique in the study area as they were formed and are hydrologically dominated by a major river. Mohave Valley between Davis Dam and Topock, the Parker, Palo Verde, and Cibola Valleys between Parker Dam and the Narrows below Cibola, and the Yuma area between Imperial Dam and the international boundary were formed during several periods of degradation and aggradation of the Colorado River (fig. 33). The flood plains, which are as much as 10 mi wide, were formed by the last aggradation of the river. The boundary between the flood plain and the terraces is the contact between the older and younger alluviums (Metzger and Loeltz, 1973; Metzger and others, 1973; Olmsted and others, 1973).

Ground-water development occurs primarily within the flood plain. Virtually all the ground water underlying the flood plain originated either as seepage from the river channel or as overbank flooding of the Colorado River. Ground-water discharge occurs primarily through evapotranspiration in the flood plain. In Parker, Palo Verde, and Cibola Valleys and the Yuma area, ground water is also discharged through artificial drains and as subsurface return flow.

The source of the ground water—the Colorado River, ultimately from central Colorado—is seen in the relation between  $\delta D$  and  $\delta^{18}O$  for selected wells in Mohave, Parker, Palo Verde, and Cibola Valleys and the Yuma area (fig. 34). The deuterium content of  $-100$  to  $-120\text{‰}$  is approximately  $60\text{‰}$  depleted in deuterium relative to precipitation that recharges the ground water along the flanks of the basins. The plot of  $\delta D$  and  $\delta^{18}O$  in figure 34 shows a departure from the meteoric water line of  $\delta D = 8\delta^{18}O + 10$  (Craig, 1961); a slope of evaporation of about 5 indicates that extensive evaporation of the Colorado River has occurred. An estimated initial deuterium content of approximately  $-120\text{‰}$  is indicative of the precipitation and runoff from central Colorado (Doe, 1983).

Deuterium, sulfate, and chloride contents of the ground water (fig. 33) suggest that recharge from the river occurs by seepage beneath the flood plain and

overbank flow. In the Mohave Valley flood plain the ground water in wells G, H, I, and J seems to have been recharged by seepage. The similarity of deuterium content of the samples ( $-104$  to  $-109\text{‰}$ ) to that of the river water ( $-106\text{‰}$ ) at Hoover Dam in 1980, the larger sulfate and chloride concentrations, and the lower sulfate to chloride ratios of the samples relative to the water at Hoover Dam are evidence. The ground water in well F, about 2.7 mi from the river at the contact of the flood plain and the piedmont slope, may have been recharged by overbank flow. The depleted deuterium content of  $-117\text{‰}$  and the small sulfate concentration of 150 mg/L suggest that recharge may have occurred during spring runoff before construction of the dam. Beginning in the early 1940's with the completion of Hoover Dam, the river has been controlled by a series of dams, and, as a result, overbank flow generally no longer occurs.

#### MOVEMENT OF WATER INTO THE PIEDMONT AREAS

In Mohave, Palo Verde, and Parker Valleys, the  $\delta D$  and  $\delta^{18}O$  of several samples indicate that water movement from the Colorado River transgresses the flood-plain deposits and extends a considerable distance into the piedmont areas. Wells B, L, and M on the piedmont slopes show mixing of flood-plain waters and ground water recharged from the basin flanks (fig. 34). The proportions of water from the Colorado River are calculated by the following equation:

$$\text{Percentage of river water} = \frac{\delta_n - \delta_x}{\delta_n - \delta_c} \times 100 \quad (32)$$

where

$n$  = ground water from basin flanks ( $\delta D = -61.25\text{‰}$ ;  $\delta^{18}O = -8.25\text{‰}$ ),  
 $x$  = sample ( $\delta D$  and  $\delta^{18}O$  of wells B, L, and M), and  
 $c$  = river water ( $\delta D = -117\text{‰}$ ;  $\delta^{18}O = -15.3\text{‰}$ ).

For ground water recharged from the basin flank, a  $\delta D$  of  $-61.25 \pm 0.9\text{‰}$  and a  $\delta^{18}O$  of  $-8.25 \pm 0.3\text{‰}$  were used; these are average values of four samples from Palo Verde and Mohave Valleys and the Yuma area. For the Colorado River, a  $\delta D$  of  $-117\text{‰}$  and a  $\delta^{18}O$  of  $-15.3\text{‰}$  (well F) were used for samples from wells L and B. These values were used for the river water because the isotopic compositions of the samples lie on a mixing line between the native ground water and these values. The isotope content of the Colorado River at Hoover Dam,  $-106\text{‰}$ , was used for the mixing calculation at well M for similar reasons. For comparison purposes, both sets of isotope values of the river water were used for the mixing calculations at well M.

The percentages of water from the Colorado River derived from both  $\delta D$  and  $\delta^{18}O$  for the calculations are shown in table 21. The  $\delta D$  and  $\delta^{18}O$  indicate that about 38

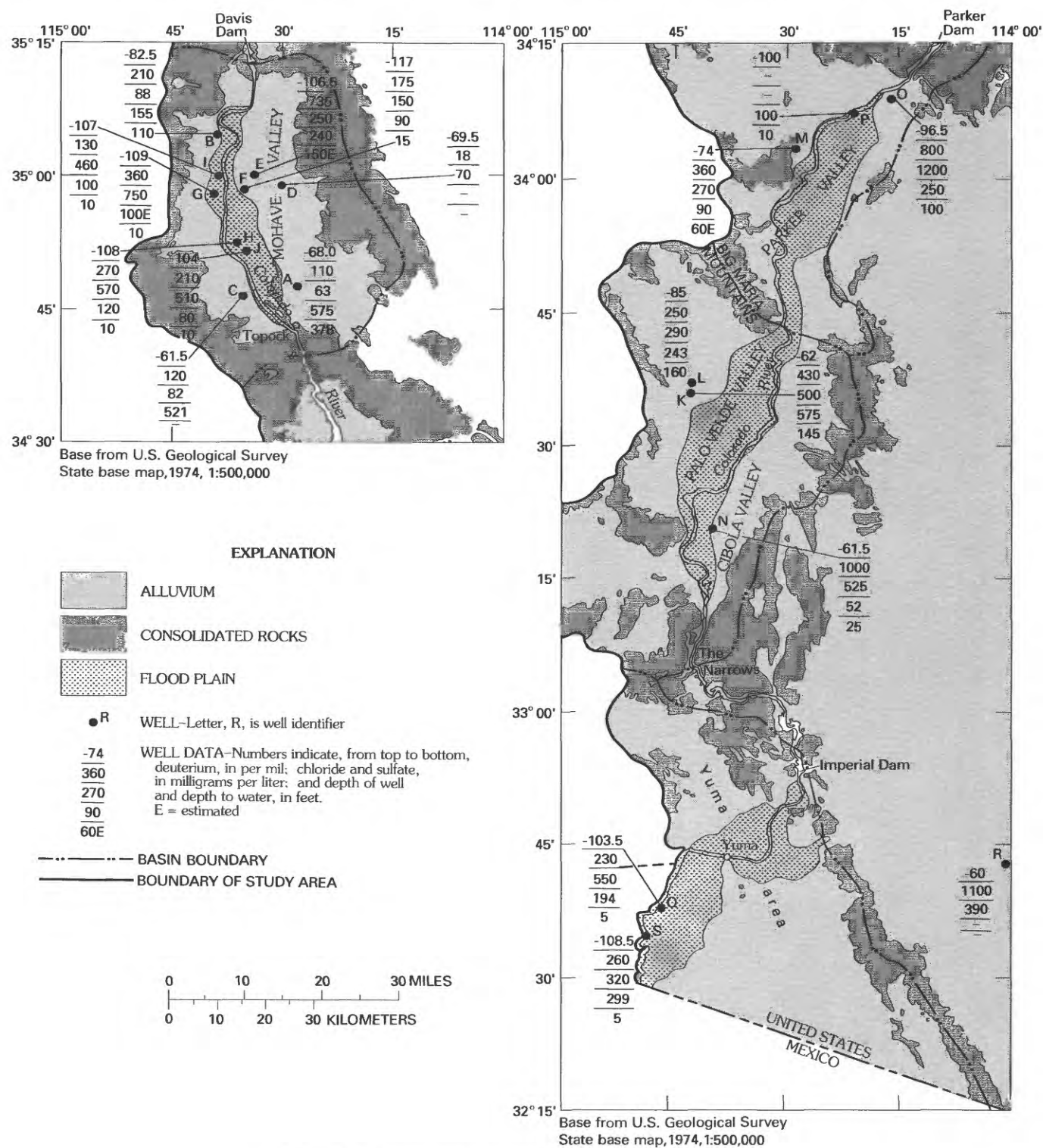


FIGURE 33.—Basins and wells sampled along the Colorado River.

percent of the water in well B and 43 percent of the water in well L originated from the river. Well M, which is less than a mile from the base of the Big Maria Mountains, receives roughly 25 percent of its water from the river. The contribution is noteworthy, as the Big Maria Moun-

tains are one of the largest ranges along the river and thus probably receive more precipitation than other nearby ranges. It is hydrologically interesting that river water is present even near the mountain-front recharge area of the basin. The interpretation of the isotope data,

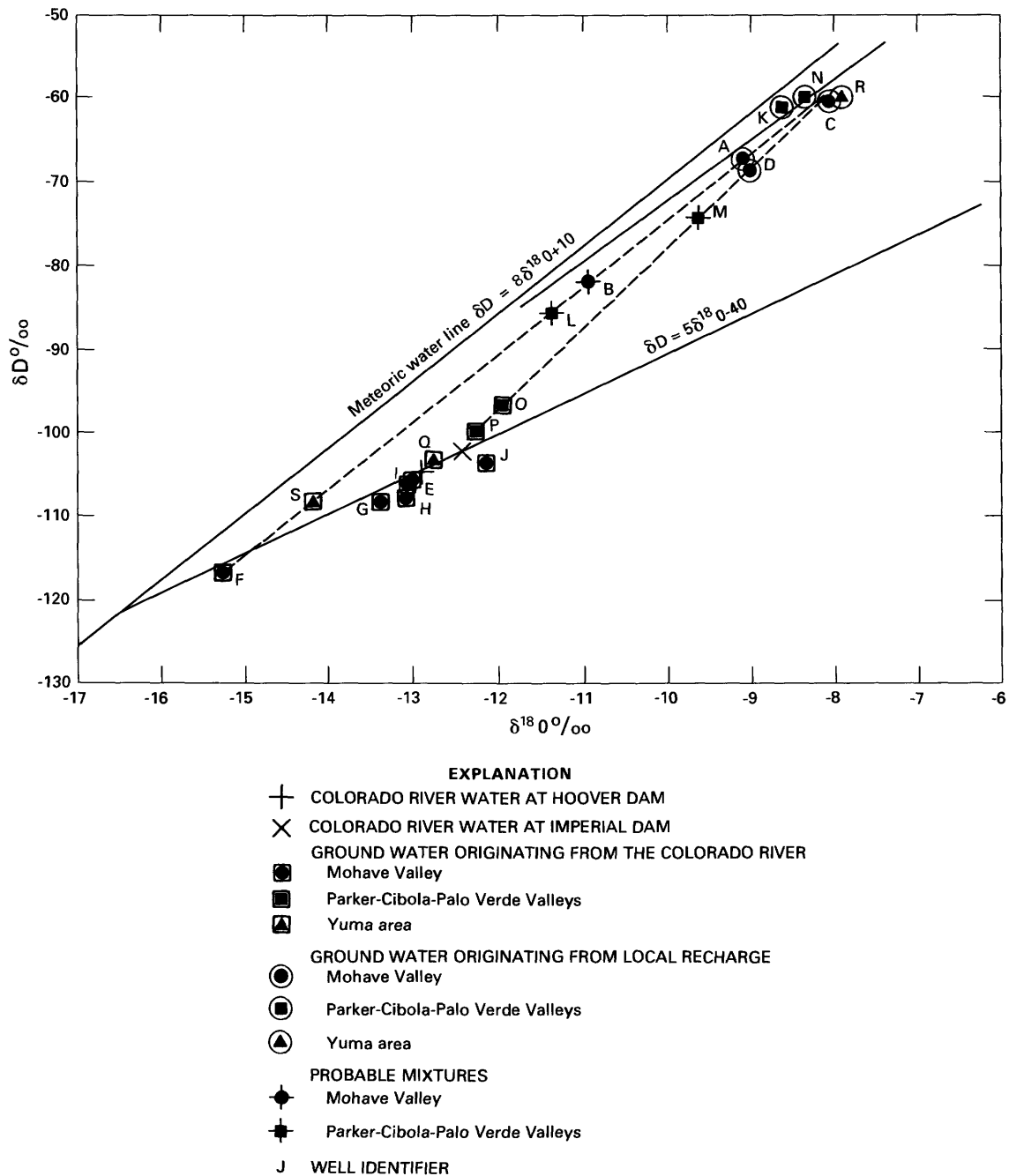


FIGURE 34.— $\delta D$  and  $\delta^{18}O$  content of Colorado River water and of ground water in basins along the Colorado River.

if valid throughout the area, indicates that significant amounts of river water are moving beyond the flood plain into the piedmont areas. Interpretations based on hydrologic data have indicated that significant amounts of water probably are not moving beyond the flood plain (Metzger and others, 1973, p. 55).

#### EVOLUTION OF THE GROUND WATER

Because infiltration of Colorado River water recharges the aquifers along the river, chemical evolution of the

ground water must be related to the river water. As will be seen, there is more than one way the ground-water composition can be derived from that of the river water. Olmsted and others (1973) concluded that the changes in the chemical characteristics of the ground water in the Yuma area were related primarily to five reactions: (1) concentration by evapotranspiration, (2) ion exchange (calcium replacing sodium on the substrate), (3) precipitation of calcium and magnesium carbonates, (4) sulfate reduction, and (5) hardening (sodium replacing calcium

TABLE 21.—Percentage of Colorado River water in wells  
[Well locations shown in fig. 33]

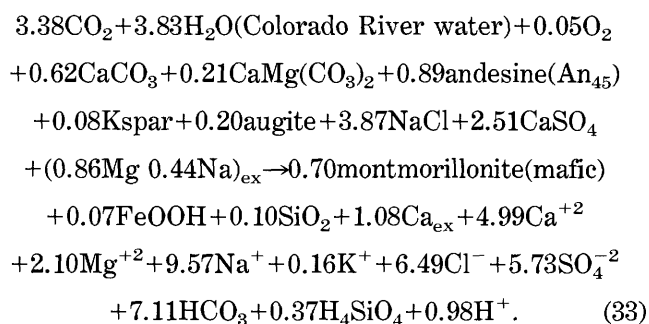
Well	$\delta D$ data	$\delta^{18}O$ data	Average
L .....	41.6	45.4	43.5
B .....	38.1	38.3	38.2
M .....	22.9	19.2	21.1
M* .....	28.5	29.0	28.8

\*Using isotope data of Colorado River at Hoover Dam.

on the substrate). Reaction 1 was required to account for the higher salinity, and reactions 3 and 4 were required to reduce the subsequent elevated sulfate and bicarbonate concentrations to observed levels. Reactions 2 and 5 were used to adjust any calcium or sodium imbalance. Metzger and Loeltz (1973) and Metzger and others (1973) also used these processes to account for the evolution of the ground water in the Needles area and the Parker-Blythe-Cibola area, respectively.

Data collected and chemical modeling done during this study were used to develop alternative processes. Two fundamental differences between Colorado River water and the ground water are the increased salinity and the lower sulfate to chloride ratios of the ground water. The sulfate to chloride ratio of the Colorado River water from 1941 to 1965 ranged from 3:1 to 5:1, the weighted-average value being about 3:1 (Olmsted and others, 1973), whereas the ground water contains much lower ratios, commonly less than 1:1. In this study, an alternate process consisting of dissolution reactions, primarily halite, is offered to account for the observed changes.

The water composition of well Q in the Yuma area (table 22) was derived from the river water using reactions and phases determined during this study. Equation 33 shows how the composition of a saline ground water in the Yuma area can be derived from the river water starting with the weighted-average analysis of the Colorado River water:



The major reactions suggested are the dissolution of halite, gypsum, calcite, and dolomite; the weathering of silicates; a decrease in pH, from soil  $\text{CO}_2$ ; and the exchange of calcium for magnesium and sodium.

Dissolution of halite, gypsum, and carbonates and weathering reactions are favored over the previously

TABLE 22.—Weighted-average analysis of Colorado River water and analysis of well Q in the Yuma area

[In millimoles per liter; values in parentheses are in milligrams per liter. Well location shown in fig. 33]

	Weighted average river water, 1941-65*	Well Q (C-9-24)19bdd, 5-20-80**
$\text{Ca}^{+2}$ .....	2.35 (94)	4.99 (200)
$\text{Mg}^{+2}$ .....	1.15 (28)	2.10 (51)
$\text{Na}^+$ .....	4.78 (110)	9.57 (220)
$\text{K}^+$ .....	.13 (5.0)	.16 (6.4)
$\text{Cl}^-$ .....	2.62 (93)	6.49 (230)
$\text{SO}_4^{-2}$ .....	3.22 (309)	5.73 (550)
$\text{HCO}_3^-$ .....	2.70 (165)	7.11 (434)
$\text{SiO}_2$ .....	.17 (10)	.37 (22)

\*Olmsted and others (1973, p. 125).

\*\*Date sampled.

cited processes because of the known geology of the area, isotopic content, high  $\text{P}_{\text{CO}_2}$ , and dissolved-oxygen content of the ground water. Equation 33 shows that the dissolution of halite alone can account for the decrease in sulfate to chloride ratios and for a major part of the increase in salinity. The low sulfate to chloride ratios of water from wells in the piedmont areas as well as on the flood plains indicate that dissolution of halite is an important reaction throughout the area. Sodium chloride or residual pore fluids of the marine Bouse Formation could readily cause an increase of chloride concentrations through upward leakage or dissolution. The Bouse Formation is observed as far north as Lake Mohave (Bentley, 1979). The lack of correlation between  $\delta D$  and sulfate and chloride supports a geologic control for the increase in chloride and sulfate concentrations. The concentrations of sulfate and the ion ratios of sulfate and chloride also do not represent a simple reduction in volume of the river water; the sulfate to chloride ratio of about 3:1 of the river water is not represented in the ground water, and at well E the ratios are reversed. The commonly observed threefold increase in bicarbonate concentrations from about 150 mg/L in the river water to 450 mg/L in the ground water can result from dissolution of carbonate minerals. Shallow depths to water of 5 to 15 ft and the abundance of vegetation may favor dissolution rather than precipitation of calcite. A constant  $\text{P}_{\text{CO}_2}$  associated with plant respiration could supply the hydrogen ions for dissolution reactions (eq. 26). Lastly, sulfate reduction probably is not occurring in the oxygenated ground water. Aquifer tests indicate that transmissivities in the Yuma area and in the Parker-Blythe-Cibola area are on the order of several hundred thousand to several million gallons per day per foot (Metzger and others, 1973, p. 68; Olmsted and others, 1973, p. 70). The water of the Colorado River is saturated with dissolved oxygen ( $\sim 10$  mg/L), and it is unlikely the sand and gravel would deplete the ground water of oxygen. The assumed oxygenated waters are supported by field data, as all

wells sampled contained dissolved oxygen. The overall data suggest that evaporation occurs before infiltration and that dissolution of halite and gypsum within the alluviums are the major reactions controlling the ground-water chemistry.

Equation 33 shows that different types of reactions can account for the observed chemistry. The reactions shown in the equation are more realistic than those cited from previous studies, but they may not fully describe the evolution of the water. For example, magnesium may have major sources other than ion exchange. Because of the differences in chemistry of the recharge waters and the differences in geology and hydrology of the Colorado River area, the reactions derived for the other basins may not be fully applicable. Because of limitations of the mineralogic and isotope data of the aquifer and the isotope data of the ground water and soil gas, all reactions could not be defined unequivocally for the basins along the Colorado River.

### SENSITIVITY ANALYSIS

The selection and composition of the phases are the most critical considerations in the development of chemical models. To provide a consistent framework for the development and transferability, several fundamental assumptions were made regarding the selection: (1) the minerals in the rocks surrounding the basins also are spatially distributed in the basin fill, (2) the compositions of individual minerals are invariant throughout and among basins, (3) the variation in compositions of individual minerals is not large, (4) relatively few phases are primarily responsible for controlling the ground-water chemistry, and (5) the phases selected for the modeling are the correct phases. During the course of the modeling, several questions arose concerning the phases:

1. Were the minerals selected or observed primary or secondary?
2. Were any minerals related to the regional flow system?
3. Are there any differences between the mineralogy or chemistry of the coarse-grained fraction versus the fine-grained fraction of the alluvium?

The dissolved constituents in the ground water that are considered in the mass-transfer calculations are  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{F}^-$ ,  $\text{Al}^{+3}$ ,  $\text{Fe}^{+3}$ ,  $\text{SiO}_2$ ,  $\text{CO}_2$ , and  $\text{O}_2$ . Although iron and aluminum are in solution only in trace amounts, they must be considered because they remain conservative in the solid phases. As the number of common minerals exceeds the number defined by the constituents, each probable phase must be tested by field and laboratory criteria and, if found invalid, eliminated. A sensitivity analysis was developed to test primary min-

erals, clay minerals, and initial water compositions systematically. Reactions were eliminated on the basis of criteria in three major categories: (1) mineralogic, (2) thermodynamic, and (3) isotopic. The reader is again referred to Plummer and others (1983) for pitfalls in selecting unique phases for models, as for most systems more than one set of phases may satisfy these or other criteria.

The selection of reactant silicate phases was based on the known mineralogy of the mountains and on the mineralogy of the sedimentary rocks in the basin fill determined through XRD data or thin-section petrography. The mineralogic information on the basin fill generated through the reconnaissance solid-species program proved invaluable in the chemical modeling. Where such data are not available (most basins), the mineralogy of the basin fill was assumed to be identical to the mineralogy of the surrounding mountains, which was estimated from information from previous studies.

Idealized formulas were adopted for the primary minerals. Fortunately, compositional variation of these minerals, particularly feldspars, is small relative to the clay minerals (Deer and others, 1976, 1980) and therefore a minimal error is introduced into the reactant side of the equations. However, clay minerals, smectites in particular, vary widely in their composition and could not be idealized from the XRD analysis or from the literature. The smectite composition was defined by establishing fixed compositions for the primary minerals and modeling reactions using end members of the smectite group and initial water compositions. The end members established brackets, or confidence intervals, of suitable smectite compositions as determined by the mass transfer.

The smectites have an enormous compositional variation through substitution of elements in the octahedral layer and the two tetrahedral layers of the 2:1 structure. Substitution of  $\text{Al}^{+3}$  ions for  $\text{Si}^{+4}$  in the tetrahedral layer causes a net deficiency of charge in the 2:1 layer, which is balanced by a cation in an interlayer position between the two tetrahedral layers. Substitution of  $\text{Mg}^{+2}$  and  $\text{Fe}^{+2}$  for  $\text{Al}^{+3}$  in the octahedral layer will also introduce cations into the interlayer position. Substitution of  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ , and  $\text{Mg}^{+2}$  for  $\text{Al}^{+3}$  or of  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ , and  $\text{Al}^{+3}$  for  $\text{Mg}^{+2}$  in the octahedral layers may be balanced by interlayer cations or by introducing vacancies in the octahedral layer (Deer and others, 1976).

The end members selected for the analysis were beidellite, nontronite, saponite, montmorillonite, and the clay mineral illite. End members were derived by substitution in the dioctahedral pyrophyllite ( $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) and trioctahedral talc ( $\text{Mg}_4\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), which may be considered the simplest structures of the smectite group. Substitutions were  $\text{Al}^{+3}$  for  $\text{Si}^{+4}$  in the tetrahedral layer of pyrophyllite (beidellite),  $\text{Fe}^{+3}$  for



TABLE 23.—Clay phases considered in the mass transfer

Phases	Stoichiometry
Beidellite .....	$\text{Na}_{0.5}\text{Al}_{2.5}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$ $\text{Ca}_{0.165}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$ $\text{Ca}_{0.25}\text{Al}_{2.5}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$
Nontronite.....	$\text{Ca}_{0.165}\text{Fe}_{2.0}\text{Al}_{0.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$
Saponite .....	$\text{Ca}_{0.165}\text{Mg}_{3.0}\text{Al}_{0.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$
Illite (sodium).....	$\text{Na}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$
Illite (potassium).....	$\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$
Montmorillonite.....	$\text{Ca}_{0.165}\text{Mg}_{0.5}\text{Al}_{1.56}\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2$ $\text{Ca}_{0.25}\text{Mg}_{0.5}\text{Al}_{1.50}\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2$

$\text{Al}^{+3}$  in the tetrahedral layer of pyrophyllite (nontronite),  $\text{Al}^{+3}$  for  $\text{Si}^{+4}$  in the tetrahedral layer of talc (saponite), and  $\text{Mg}^{+2}$  for  $\text{Al}^{+3}$  in the octahedral layer of pyrophyllite (montmorillonite). Two formulas for the mineral illite were used to represent the clay-sized minerals belonging to the mica group. Small compositional variations were made within these end members to affect a range of the interlayer charge between 0.33 and 0.50. Calcium, sodium, and potassium were used as interlayer cations. The phases and stoichiometry are given in table 23.

The primary minerals of the mafic model were reacted with the recharge water and variations of the recharge water using the selected clay end members. The composition of the recharge water was varied, maintaining electrical neutrality, within the standard deviation of sodium and bicarbonate, calcium and bicarbonate, and sodium and calcium. The magnesium and calcium contents of the carbonate phase were varied from a nearly pure dolomite to pure calcite (60-, 80-, and 100-mol percent calcium). Thus, each model with a clay end member represents at least 21 reactions. The results are summarized in table 24.

Each reaction was examined for validity against the three categories of criteria cited earlier. In table 24, a checkmark is entered for a reactant or product phase if the reaction is consistent. "Diss" or "ppt" signifies that a phase is dissolving or precipitating in violation of thermodynamic constraints. "L" signifies that a phase is dissolving or precipitating in compliance with thermodynamic constraints but that the mass transfer is exceedingly large, thereby violating mineralogic and chemical constraints. "I" signifies that the derived isotopic composition of the  $\text{CO}_2$  gas is too light, and "h" too heavy, as dictated by isotopic constraints. A derived  $\delta^{13}\text{C}$  of greater than  $-14\text{‰}$  and less than  $-22\text{‰}$  was considered unacceptable. On the basis of the agreement of the derived mass transfer with these constraints, a reaction is designated either unacceptable or acceptable by "U" or "A." In all cases, reactions considered unacceptable had violated more than one constraint.

The sensitivity analysis shows that three compositions or their variations are suitable phases: a dioctahedral

beidellite, a dioctahedral montmorillonite, and a potassium-rich illite. Although beidellite does not contain magnesium, an acceptable mass transfer was derived because its composition is similar to that of montmorillonite. The absence of magnesium in beidellite can be compensated for by dissolution of dolomite. However, beidellite becomes an unacceptable phase in computing mass transfer in basins because dolomite is not present as a reactant or product.

The analysis revealed several general trends. Calcium is the major interlayer cation; potassium also probably is in the interlayer position. The variation of the interlayer charge from 0.33 to 0.50 does not affect the model, as the mass transfer derived is virtually identical in this range. The model is most sensitive to variations in magnesium, but, surprisingly, the variation in aluminum between 1.56 and 2.33 atom has no dramatic effect that is not compensated for by compositional variations of the smectite. On the basis of the results of the analysis, a smectite composition that fell within the limits of the three suitable phases was selected for the modeling. Additional reactions were subsequently run for final adjustment of the magnesium content of the carbonate phase for compliance with the three constraints, particularly the  $\delta^{13}\text{C}$  mass balance. More than 200 mineral assemblages among 27 phases that were deemed realistic were considered in development of the recharge models. Under assumptions set forth at the beginning of this section, the stoichiometries derived for minerals in the recharge model thus also became those used in the modeling of the basins.

## CLAY MINERALOGY

Near the end of the study, four clay samples (less than 2- $\mu\text{m}$  fraction) from three basins were selected for structural formula determination, as some detailed information on the smectite was desirable for testing the conclusions and assumptions of the chemical models. The samples selected were those showing the least content of mica, kaolinite, and mixed layering as determined by the XRD analyses. The chemical analyses of the four samples are shown in table 25, and the formulas determined from the analyses are shown in table 26. Because sodium phosphate and sodium chloride were used in the separation procedures and are abnormally high, the analyses are shown recalculated without sodium and phosphorus. The structural formulas of the field-determined clay samples are those of an end member montmorillonite and are similar to the formulas determined by the sensitivity analysis. The major differences between the field- and model-derived montmorillonites are lower  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratios and higher  $\text{Fe}_2\text{O}_3/\text{MgO}$  ratios.

Any conclusions based on four samples are tenuous, particularly in the absence of sodium data and possible

TABLE 24.—*Sensitivity analysis and summary of mass-transfer calculations*

[In millimoles per liter; ✓, reactant is consistent; ppt, precipitating; diss, dissolving; L, abnormally large; l, derived  $\delta^{13}\text{C}$  too light; h, derived  $\delta^{13}\text{C}$  too heavy; U, unacceptable; A, acceptable. Dashes indicate element not used]

Clay mineral	Mineral phase	Recharge water*			Variation in composition of recharge water*								
		Variation of interlayer charge			Variation of $\text{Na}^+$ and $\text{HCO}_3^-$			Variation of $\text{Ca}^{+2}$ and $\text{HCO}_3^-$			Variation of $\text{Ca}^{+2}$ and $\text{Na}^+$		
		(Na) 0.5	(Ca) 0.165	(Ca) 0.25	$\text{Na}^+$ $\text{HCO}_3^-$	0.30 4.14	1.64 5.48	$\text{Ca}^{+2}$ $\text{HCO}_3^-$	1.61 4.14	2.28 5.48	$\text{Ca}^{+2}$ $\text{Na}^+$	1.60 1.66	2.29 0.28
Beidellite .....	Plagioclase	L	✓	✓		ppt	L		✓	✓		L	ppt
	K-spar	✓	✓	✓		✓	✓		✓	✓		✓	ppt
	Augite	✓	✓	✓		✓	✓		✓	✓		✓	✓
	FeOOH	✓	✓	✓		✓	✓		✓	✓		✓	diss
	Smectite	L	✓	✓		diss	L		✓	✓		L	diss
	$\text{SiO}_2$	✓	✓	✓		✓	✓		✓	✓		✓	✓
	$\delta^{13}\text{C}$	h	✓	✓		✓	h		✓	✓		h	✓
	Summary	U	A	A		U	U		A	A		U	U
Saponite .....	Plagioclase	—	✓	—		ppt	L		✓	✓		L	ppt
	K-spar	—	✓	—		✓	✓		✓	✓		✓	✓
	Augite	—	ppt	—		L	ppt		ppt	ppt		L	L
	FeOOH	—	diss	—		L	diss		diss	diss		diss	✓
	Smectite	—	diss	—		✓	diss		diss	diss		diss	L
	$\text{SiO}_2$	—	L	—		L	L		L	L		L	L
	$\delta^{13}\text{C}$	—	h	—		h	h		h	h		h	h
	Summary	—	U	—		U	U		U	U		U	U
Nontronite.....	Plagioclase	—	✓	—		ppt	L		✓	✓		L	ppt
	K-spar	—	✓	—		✓	✓		✓	✓		✓	✓
	Augite	—	✓	—		✓	✓		✓	✓		✓	✓
	FeOOH	—	diss	—		L	diss		diss	diss		diss	L
	Smectite	—	L	—		diss	L		L	L		L	diss
	$\text{SiO}_2$	—	L	—		L	L		L	L		L	L
	$\delta^{13}\text{C}$	—	✓	—		L	l		✓	✓		✓	✓
	Summary	—	U	—		U	U		U	U		U	U
Illite (sodium)....	Plagioclase	—	L	—		ppt	L		L	L		L	ppt
	K-spar	—	L	—		ppt	L		L	L		L	ppt
	Augite	—	L	—		ppt	L		L	L		L	ppt
	FeOOH	—	✓	—		diss	✓		✓	✓		✓	diss
	Mica	—	L	—		diss	L		L	L		L	diss
	$\text{SiO}_2$	—	L	—		L	L		L	L		L	L
	$\delta^{13}\text{C}$	—	h	—		l	h		h	h		h	l
	Summary	—	U	—		U	U		U	U		U	U
Illite (K).....	Plagioclase	—	✓	—		ppt	L		✓	✓		L	ppt
	K-spar	—	✓	—		ppt	L		✓	✓		L	ppt
	Augite	—	✓	—		✓	ppt		L	✓		L	✓
	FeOOH	—	✓	—		✓	L		✓	✓		✓	✓
	Mica	—	✓	—		diss	L		✓	✓		L	diss
	$\text{SiO}_2$	—	✓	—		✓	L		L	✓		L	✓
	$\delta^{13}\text{C}$	—	✓	—		l	h		h	✓		h	✓
	Summary	—	A	—		U	U		U	A		U	U
Montmorillonite..	Plagioclase	—	✓	✓		ppt	L		✓	✓		L	✓
	K-spar	—	✓	✓		✓	✓		✓	✓		✓	✓
	Augite	—	✓	✓		✓	L		✓	✓		L	✓
	FeOOH	—	✓	✓		✓	L		✓	✓		✓	✓
	Smectite	—	✓	✓		diss	L		✓	✓		L	✓
	$\text{SiO}_2$	—	✓	✓		✓	✓		✓	✓		✓	✓
	$\delta^{13}\text{C}$	—	✓	✓		l	h		✓	✓		h	✓
	Summary	—	A	A		U	U		A	A		U	A

\*See table 2 for composition of recharge waters.



TABLE 25.—*Chemical analyses of four clay samples from selected basins*

[In weight percent. Analyses by Center for Meteorite Studies, Arizona State University]

	Well number and location and depth of sample below land surface			
	(B-2-2)34beb West Salt River Valley Depth, 330 feet	(D-16-25)4edd Willcox basin near playa Depth, 400 feet	(D-2-8)26caa East Salt River Valley Depth, 802 feet	(D-2-8)26caa East Salt River Valley Depth, 903 feet
MgO .....	5.51	4.06	5.67	4.97
Al <sub>2</sub> O <sub>3</sub> .....	18.04	19.10	16.90	18.08
SiO <sub>2</sub> .....	62.43	62.52	65.15	63.77
K <sub>2</sub> O .....	1.19	2.44	1.38	2.08
CaO .....	3.02	2.88	2.59	3.01
TiO <sub>2</sub> .....	.39	.54	.39	.50
MnO .....	.10	.08	.16	.07
Fe <sub>2</sub> O <sub>3</sub> .....	9.32	8.38	7.76	7.52

inclusion of noncrystalline iron and silica, but support is provided for the major assumptions set forth for the modeling. The composition of the clays suggests that the clay mineralogy indeed may be spatially invariant within and among basins throughout the area. The samples represent a range of basin types, from a basin having the highest altitude and precipitation (Willcox) to one having

low altitude and precipitation (West Salt River Valley), each showing distinct differences in vegetation, climate, geology, and hydrology. The chemical analyses of the bulk rock support the assumptions that the clays are a sink for magnesium and a partial sink for iron and that aluminum generally is conserved in the silicate phase.

Chemical analyses of the bulk-rock fraction of core from well (D-2-8)26caa in East Salt River Valley are shown in table 27 with and without sodium and phosphorus. The clay analyses of the same well (table 25) show an enrichment of magnesium of about a factor of two relative to the bulk-rock samples. The enrichment of iron appears to be somewhat less than two. Aluminum appears to be generally conserved but is slightly depleted relative to the initial primary phases and slightly enriched relative to the bulk-rock fraction. Chemical analyses of the bulk-rock fraction of core from two additional wells, (A-1-7)36daa2 and (D-6-9)29bba, in East Salt River Valley are shown in table 27 to illustrate the similarity and spatial variation in sediment chemistry. Calcium in particular varies vertically owing to the presence of calcite, which is indicated by the large losses on ignition of samples from the lowest interval of well (D-2-8)26caa. Wells (D-2-8)26caa and

TABLE 26.—*Structural formulas and location of four clay samples*

Location	Atoms per 2:1 phyllosilicate half cell										
	Tetrahedral			Octahedral						Interlayer	
	Si	Al	Total tetrahedral	Mg	Al	Fe	Mn	Ti	Total octahedral	Ca	K
(B-2-2)34bcb West Salt River Valley .....	3.82	0.18	4.00	0.50	1.12	0.43	0.01	0.01	2.07	0.19	0.09
(D-16-25)4cdd Willcox basin near playa.....	3.82	.18	4.00	.37	1.20	.39	.01	.03	2.00	.18	.19
(D-2-8)26caa East Salt River Valley, Depth 802 feet ...	3.94	.06	4.00	.51	1.15	.35	.01	.01	2.04	.17	.11
(D-2-8)26caa East Salt River Valley, Depth 903 feet ...	3.88	.12	4.00	.45	1.18	.34	.01	.02	2.02	.19	.16

TABLE 27.—*Chemical analyses of the bulk-rock fraction of core from selected wells in East Salt River Valley*

[In weight percent. Analyses by Center for Meteorite Studies, Arizona State University. Dashes indicate element not included]

	(D-2-8)26caa								(A-1-7)36daa2						(D-6-9)29bba							
	Depth,* 375 feet		Depth,* 712 feet		Depth,* 1,102 feet		Depth,* 1,600 feet		Depth,* 100 feet		Depth,* 595 feet		Depth,* 1,021 feet		Depth,* 306 feet		Depth,* 708 feet		Depth,* 1,203 feet		Depth,* 1,799 feet	
Na <sub>2</sub> O . . .	1.82	—	1.43	—	2.06	—	1.73	—	2.13	—	2.39	—	1.99	—	1.72	—	1.68	—	3.08	—	2.79	—
MgO . . . .	2.28	2.60	3.31	3.68	2.41	2.62	1.79	2.11	2.49	2.78	3.22	3.55	2.40	2.82	2.24	2.66	4.76	5.39	1.49	1.63	2.66	2.87
Al <sub>2</sub> O <sub>3</sub> . . .	10.95	12.54	13.88	15.44	12.31	13.36	9.24	10.94	11.72	13.05	14.42	15.89	12.60	14.82	11.83	14.05	12.47	14.11	12.88	14.12	13.84	14.97
SiO <sub>2</sub> . . . .	61.84	70.78	59.46	66.16	65.31	70.90	47.82	56.60	63.08	70.26	60.59	66.80	50.96	59.93	50.34	59.77	54.81	62.05	65.49	71.81	60.73	65.70
P <sub>2</sub> O <sub>5</sub> . . . .	.24	—	.28	—	.23	—	.11	—	.26	—	.30	—	.22	—	.25	—	.33	—	.21	—	.32	—
K <sub>2</sub> O . . . .	2.63	3.00	3.08	3.43	2.99	3.43	2.14	2.53	2.31	2.57	2.27	2.54	2.16	2.55	2.67	3.16	3.28	3.72	3.50	3.85	3.27	3.53
CaO . . . .	5.10	5.84	3.89	4.33	4.13	4.48	18.84	22.28	4.94	5.50	4.54	5.00	12.60	14.82	12.06	14.32	6.62	7.50	4.46	4.89	5.46	5.90
TiO <sub>2</sub> . . . .	.66	.76	.71	.79	.63	.69	.55	.65	.73	.82	.73	.80	.52	.60	.60	.71	.68	.76	.45	.50	.79	.84
MnO . . . .	.04	.05	.08	.08	.06	.07	.07	.08	.06	.07	.07	.08	.06	.07	.09	.10	.11	.13	.06	.07	.11	.11
Fe <sub>2</sub> O <sub>3</sub> . . .	3.87	4.43	5.47	6.09	4.27	4.63	4.07	4.82	4.45	4.96	4.87	5.35	3.72	4.38	4.40	5.22	5.61	6.34	2.86	3.14	5.60	6.06
LOI** . .	6.63	—	7.16	—	6.04	—	17.22	—	6.51	—	7.20	—	13.91	—	12.48	—	9.18	—	4.05	—	4.49	—

\*Depth of sample below land surface.

\*\*LOI = Percent loss on ignition.

TABLE 28.—Mass transfer derived using structural formulas of four clay samples

[Values\* in millimoles per kilogram H<sub>2</sub>O; Vek, Vekol Valley; well names keyed to fig. 15]

Phases	Flow path and reaction number**			
	1	2	3	4
O <sub>2</sub> .....	0.41	0.45	0.40	0.31
CO <sub>2</sub> .....	-.60	-.60	-.60	-.60
Calcite .....	-3.49	-3.49	-3.49	-3.49
Andesine (An <sub>45</sub> ) .....	3.56	3.36	3.70	3.92
Potassium feldspar .....	.54	.67	.95	1.10
Augite .....	2.34	2.57	2.31	1.77
Silica .....	2.99	4.28	3.57	3.11
Halite .....	1.63	1.63	1.63	1.63
Gypsum .....	.77	.77	.77	.77
Fluorite .....	.01	.01	.01	.01
Montmorillonite .....	-4.75	-5.01	-5.21	-5.17
Goethite .....	.40	-.05	.16	.78
Ion exchange† .....	.55	.60	.51	.45

\*Reactants are positive and products are negative.

\*\*Indicates location of clay sample: 1, (B-2-2)34bcb; 2, (D-2-8)26caa (802); 3, (D-2-8)26caa (903); 4, (D-16-25)4cdd.

†Calcium replacing sodium on the substrate.

(A-1-7)36daa2 are near the recharge area of the Superstition Mountains, and well (D-6-9)29bba is in the basin center between Casa Grande and Florence. The chemical analyses of samples from depth intervals shown in table 27 suggest that if differences in sediment chemistry exist, they may be greater in the vertical dimension than in the horizontal.

#### MASS TRANSFER OF OXYGEN AND SILICA

The modeling and the field-determined montmorillonites suggest that a typical montmorillonite composition observed in Arizona may have lower Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratios than those derived by the modeling but that the amount formed will be more in accord with the higher Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio. In other words, less montmorillonite is formed from weathering a given amount of rock than is indicated by the observed smectite composition, assuming conservation of aluminum. The mass transfer determined by using the model-derived montmorillonite with the higher ratio appears more compatible with the chemical and mineralogic data when stoichiometry constraints of the ferromagnesian minerals, dissolved-oxygen content in the ground water, and possibly silica content of the ground water are considered.

Reactions 1, 2, 3, and 4 in table 28 show the mass transfer in Vekol Valley using the formulas of the four montmorillonite samples from table 26. The oxidation of iron in augite using all formulas depletes the ground water of dissolved oxygen, total consumption ranging between 12 and 17 mg/L. The graph of dissolved oxygen

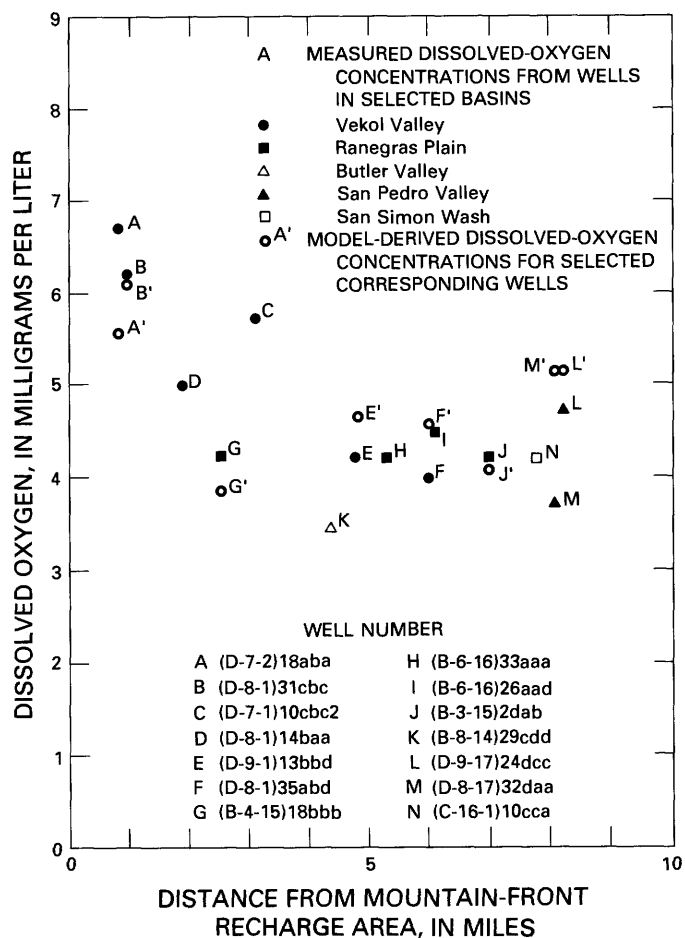


FIGURE 35.—Measured and model-derived concentrations of dissolved oxygen from wells in selected basins.

and distance along flow paths shown in figure 7 is illustrated again in figure 35, showing the agreement of measured dissolved-oxygen concentrations with model-derived concentrations. The model-derived concentrations are computed from the total consumption of dissolved oxygen along the flow path. The total consumption is defined as the amount of oxygen required to oxidize Fe<sup>+2</sup>, presumably the only reductant in the hydrochemical system, from the time of infiltration of water to the final water. The initial dissolved-oxygen content of the ground water at the time of infiltration is placed at 11 mg/L, which would be the amount in the ground water at saturation at 10 °C and 3,000-ft altitude, an estimated average temperature and altitude for winter recharge of the basin lowlands. This value is also in good agreement with field measurements of dissolved oxygen in streams, as listed in table 9.

The mass transfer of silica also places a limit on the amount of montmorillonite formed. The modeling of the basins using all montmorillonite compositions indicates that silica is controlled primarily by the clay phase. Silica

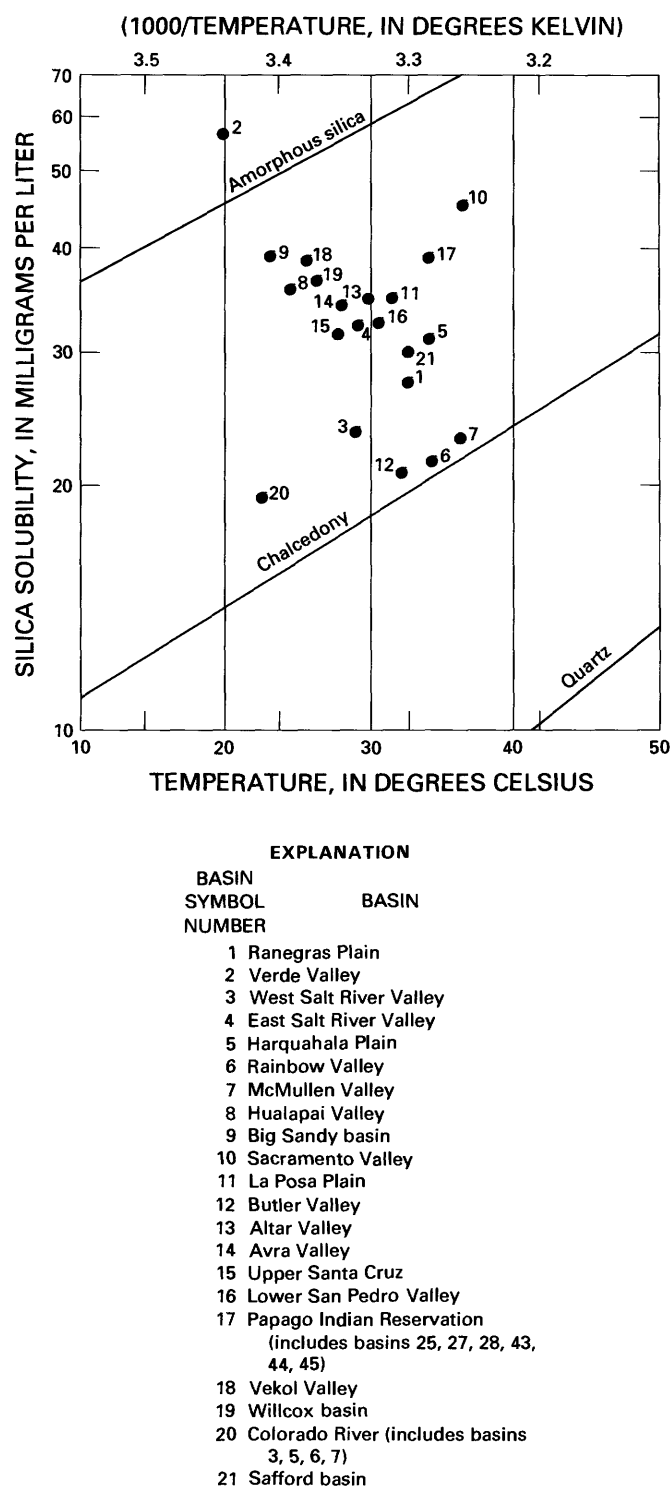


FIGURE 36.—Relation of average silica concentrations in ground water from selected basins to silica minerals and temperature.

released to the aqueous phase through silicate weathering in Vekol Valley, for example, is about 12.0 mmol, of which montmorillonite removes about 90 percent. A small change in the silica composition of the montmoril-

lonite may require control by an additional phase or a source of additional silica. For example, an increase in silica in montmorillonite from 3.65 to 3.82 atoms would require dissolving at least 3 mmol (180 mg/L) of additional silica. Dissolving this amount of silica is unlikely because of the low solubility of quartz, the most abundant silica source.

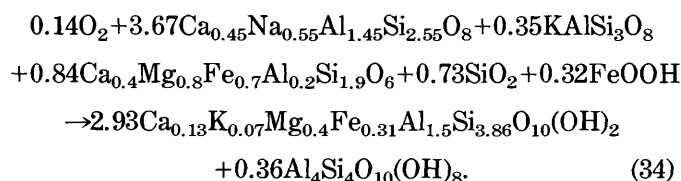
Silica may not be dissolving but, as indicated by the modeling, may be precipitating along the flow path. Average silica concentrations in ground water from several basins and the solubilities of amorphous silica, chalcedony, and quartz are shown in figure 36. Wells sampled in the Big Sandy and Willcox basins and in Hualapai, Vekol, and Sacramento Valleys are near recharge areas. Wells sampled in Ranegras and Harquahala Plains and in lower San Pedro, Butler, McMullen, and Rainbow Valleys are near the center or along the axis of the basin and represent downgradient waters. The trend in silica concentrations along the chalcedony phase boundary suggests that chalcedony may be an additional minor control for removal of silica.

The interpretations using the depletion of dissolved oxygen in support of the models are valid under the following assumptions: (1) most of the iron in the ferromagnesian minerals is  $\text{Fe}^{+2}$ , (2) the unoxidized iron and magnesium mole ratios of the minerals are near unity, (3) the less than 62- $\mu\text{m}$  fraction adequately reflects the bulk-rock chemistry of the basin fill, (4) no additional reductants are present in the aquifer, and (5) the initial dissolved-oxygen concentration of the ground water at the time of recharge is about 10 to 12 mg/L. Assumptions 1 and 2 regarding the oxidation state and content of the iron are the weakest. Primary minerals are known to contain some  $\text{Fe}^{+3}$  and, as was discussed earlier in the section on reactions in the unsaturated zone, the ferromagnesian minerals are preferentially leached relative to other minerals. The basic assumptions that the proper minerals have been identified and that the derived mass transfer is correct also apply to the above interpretation.

#### MASS TRANSFER OF KAOLINITE

The apparent smaller mass transfer of montmorillonite may be related to the geochemical behavior of aluminum and its distribution in the basin. One explanation may be that the rocks of the mountains contain less aluminum than the idealized mineral phases. The aluminum content of the selected silicate phases is greater than that indicated by chemical analyses of the bulk rock (less than 62- $\mu\text{m}$  fraction) of the basin fill, supporting the depletion of aluminum (tables 5, 6, 27). Alternately, aluminum may be conserved in aluminum oxyhydroxides or, more likely, in additional secondary aluminosilicates. Supporting the oxyhydroxides, the saturation state of the ground

water is at equilibrium with respect to boehmite and is at supersaturation with respect to diasporite and gibbsite. The amount of any aluminum oxyhydroxides forming should be small, however, as these minerals are not stable under equilibrium conditions with kaolinite and montmorillonite in the quartz-rich environment. Kaolinite ( $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ ), another aluminosilicate, however, can be in equilibrium with montmorillonite. The mass transfer of the silicates and oxides along the flow path in Vekol Valley using kaolinite as an additional secondary clay mineral and a lower  $\text{Al}_2\text{O}_3/\text{SiO}_2$ -higher  $\text{Fe}_2\text{O}_3/\text{MgO}$  montmorillonite is shown in the following equation:



The reactions in equation 34 not only satisfy the aluminum balance but also alleviate the problem of silica. A reduction in the amount of precipitated or dissolved silica is more compatible with the kinetic behavior of silica. The subsequent conservation of aluminum among all primary and secondary silicates supports the major modeling assumptions. The inclusion of about 10 percent of kaolinite as an additional phase is compatible with the low  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio of the field montmorillonite and, with the exception of the amount of precipitated silica, is consistent with the derived mass transfer presented in this paper.

The questions concerning the small discrepancies in iron and silica in equation 34 will require more precise analysis of the crystalline iron and silica content of the montmorillonite. For example, a reduction in the iron content of montmorillonite from 0.32 to 0.20 atom would affect the formation and not the dissolution of goethite. Similarly, a small decrease in the mass transfer of montmorillonite or in the silica content of montmorillonite would affect silica precipitation. An excess of aluminum in kaolinite over that required for the theoretical lattice or the presence of aluminum oxyhydroxides would require even smaller amounts of kaolinite and also would minimize any problem of both silica and goethite. Resolving any differences in aluminum content among the primary rock, basin fill, and derived phases will require more knowledge of the mineralogy and chemistry of different fractions of the basin fill.

## ION EXCHANGE

The imbalance of charge in smectite structures through substitution in the octahedral and tetrahedral sites causes the smectite substrate to attract other ions

on its surface or to incorporate cations within the interlayer position. Among the cations, a preferential concentration of the multivalent cations occurs in these interlayer exchange positions because of their higher charge. This preferential exchange (selectivity) increases markedly with increased dilution of the water. The laws of mass action and thermodynamic relations have been applied in approaches regarding treatment of ion-exchange equilibrium (Thorstenson and others, 1979; Stumm and Morgan, 1981). During this study, ion exchange was treated in a concept of mass transfer, mineral phases, and water compositions.

The reaction modeling has shown that ion exchange is not a significant reaction in the ground water in most basins. In dilute waters, exchange accounts for little, if any, solute sodium, the major ion replaced on the substrate, although these dilute waters are sodic in composition. In basins that contain large concentrations of dissolved solids and sulfate, however, ion-exchange reactions have a significant impact on the water chemistry.

The absence of ion-exchange reactions in most basins can be explained by the composition of the soils, smectite, and ground water. Owing to the ubiquitous presence of calcite in soils and dissolved calcium in recharge waters, the divalent calcium ion is preferentially concentrated over sodium and potassium in the interlayer position of the smectite. Although ground water initially high in calcium evolves into a sodic water, the water remains too low in ionic strength to reduce the selectivity of the divalent cation in either the authigenic or the detrital clay. Calcium that enters the aqueous phase through hydrolysis is dissipated at the weathering rate through calcite precipitation or uptake of newly formed authigenic clay. Concentrations of calcium do not reach levels at which they may effect an exchange for sodium, potassium, or magnesium ions, which probably also are present in small amounts in the interlayer position. If large concentrations of calcium suddenly enter the aqueous phase, such as by dissolution of gypsum, all three cations may be exchanged and transferred to the dissolved phase.

## SODIUM

As determined in the modeling of Ranegras Plain, ion-exchange reactions were influential in the evolution of the high-sodic ground water. Examining the analytical data of Ran 2 and Ran 3 in Ranegras Plain again, the increase of 1.31 mmol of sodium between Ran 2 and 3 accompanied by an increase of only 0.56 mmol of chloride is difficult to explain without an ion-exchange mechanism or an unrealistic mass transfer of the silicates. At Ran 4, which is in an area of larger dissolved-solids concentrations in the northern part of the basin, the ground water

contains 41.3 mmol of sodium, 22.6 mmol of chloride, and 19.8 mmol of sulfate (table 10). Well (B-6-16)25bbc about 1 mi upgradient from Ran 4 contains 14.8 mmol of sodium, 7.9 mmol of chloride, and 4.5 mmol of sulfate. Well (B-6-16)25bbc is 1,000 ft deep; Ran 4 is 1,100 ft deep and apparently penetrates more of a buried playa deposit. An increase of 11.8 mmol of sodium in the ground water over that of the chloride increase between the two wells indicates that ion exchange is an extremely important reaction in the evolution of the water. The exchange of more than 10 mmol of sodium indicates an availability of exchangeable sodium.

The basin-fill sediments in Vekol Valley and East Salt River Valley contain an abundance of sodium (tables 6, 27). Presumably, a small amount of this sodium is situated in the interlayer position of the montmorillonite, although most of the sodium present in the basin fill probably is incorporated in minerals other than clays. Sodium in primary minerals is suggested by the vertical distribution of sodium in Vekol Valley, where the highest content is found in the sandy gravels of the lower unit, which is predominantly quartz and feldspar. The upper silt-clay unit, however, also contains appreciable sodium. Leachate analyses of drill cuttings and core from the wells indicate that the basin fill is low in chloride, and thus halite is not a major source of sodium.

#### POTASSIUM

Potassium presented difficulties in relating water compositions to specific rock-water reactions because of lower concentrations than would be expected from weathering of the source rocks. The geochemistry of potassium requires two fundamental considerations: (1) silicate minerals weather at different rates and (2) potassium may exchange for other cations on clay minerals. Minerals that form first in the crystallization series are unstable in the weathering environment (Goldich, 1938). In the case of feldspars, stability increases with increasing sodium and potassium content; potassium feldspar and muscovite are relatively stable minerals. Colman (1982), in a study of chemical weathering of rinds of basalts and andesites, determined that volcanic glass was the least stable phase and that pyroxene and plagioclase have intermediate stabilities. Potassium feldspar and the opaque minerals were resistant to weathering but did eventually weather completely. The relative elemental mobilities determined by Colman (1982) were  $\text{Ca} \geq \text{Na} > \text{Mg} > \text{Si} > \text{Al} > \text{K} > \text{Fe} > \text{Ti}$ , showing that calcium is the most mobile and titanium the least.

The average potassium concentration determined for recharge areas is small, 0.05 mmol (2.0 mg/L), but it varies significantly and may increase downgradient severalfold or may remain the same. Potassium correlates

positively ( $p < 0.0001$ ) with calcium, sodium, magnesium, chloride, sulfate, and dissolved solids in several basins. Average sulfate and potassium concentrations in basins that contain sulfate concentrations greater than 200 mg/L are plotted in figure 37. The general trend in these basins is that potassium concentrations increase downgradient with increasing sulfate concentrations. In La Posa Plain and McMullen, Vekol, and lower San Pedro Valleys, where average sulfate concentrations are small (less than 50 mg/L), the potassium concentrations also are small (2–4 mg/L) and do not increase downgradient or show significant correlations with sulfate or other major elements.

The increase in the concentrations of potassium downgradient, if caused by a mineral source, would require weathering of potassium feldspar or possibly biotite, the other source of potassium. The long residence time, the variability of potassium concentrations, and the differing saturation state of the ground water with respect to potassium feldspar tend to diminish the importance of potassium feldspar as a source. The difficulties in nucleation of potassium feldspar and its instability with respect to montmorillonite would discount the precipitation of potassium feldspar (White, 1979). The diminishing weathering rate of the ferromagnesian minerals downgradient tends to discount biotite. Removal of potassium by the clay minerals, as suggested by the statistical trends, is the likely control rather than the weathering or forming of primary or secondary minerals.

#### MAGNESIUM

In addition to weathering and precipitation reactions, magnesium may be controlled by ion-exchange reactions. In the study area, magnesium correlates positively ( $p < 0.001$ ) with calcium, dissolved solids, potassium, sulfate, sodium, and chloride. Except for the correlation with calcium, the positive correlations are the reversal of the negative correlations determined in Vekol Valley and other basins containing dilute, low-sulfate water. In Vekol Valley, for example, magnesium correlated positively with calcium and alkalinity but negatively with sodium, sulfate, chloride, dissolved solids, and pH in accordance with the aforementioned reactions. The ground water contains small sulfate concentrations and, accordingly, small magnesium concentrations (1–4 mg/L).

Magnesium correlates positively with sodium, sulfate, chloride, and dissolved solids ( $p < 0.0001$ ) in the ground waters of Ranegras Plain, Verde Valley, the Safford basin, East and West Salt River Valleys, and basins along the Colorado River. As these basins contain the largest concentrations of sulfate and magnesium, the strong correlations with salinity and sulfate suggest that

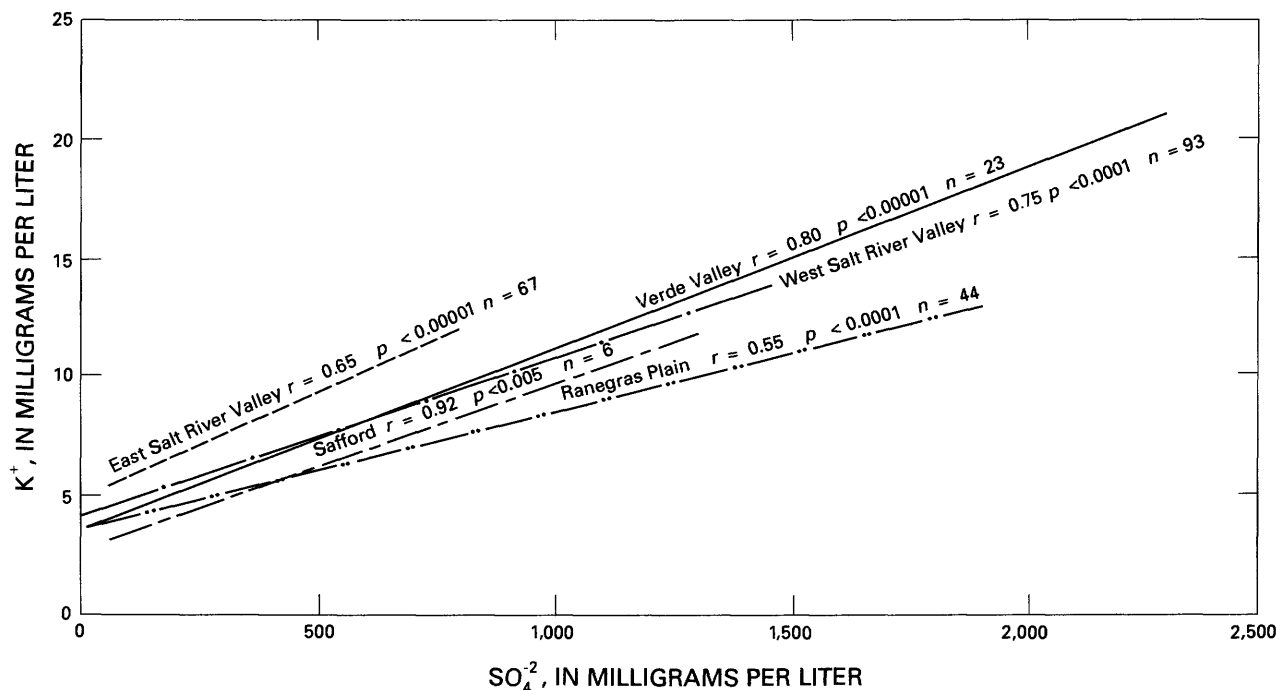


FIGURE 37.—Relation of potassium to sulfate for selected basins.

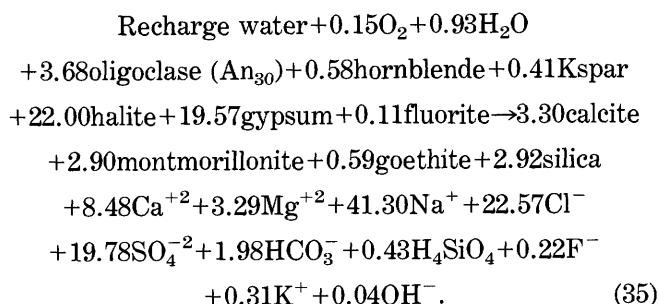
ion exchange is a major control of magnesium. As demonstrated later, ion-exchange reactions dominate the chemistry in these basins to the extent that they totally mask the fundamental reactions controlling the mass transfer of the primary and secondary silicate minerals of magnesium. The critical aspects of the basin selection for modeling are clearly revealed by the ion-exchange constraints.

Magnesium normally resides in the octahedral site of the montmorillonite; however, some magnesium seems to be available for exchange in the interlayer position. Exchangeable magnesium is inferred by the formula derived by the modeling and the formulas determined for the dioctahedral montmorillonites in table 26. The number of octahedral atoms exceeds two and suggests that some magnesium may be present in the interlayer site (Jones and Weir, 1983). In areas that contain large dissolved-solids and sulfate concentrations, the magnesium may be replaced by calcium, causing the observed large concentrations of dissolved magnesium.

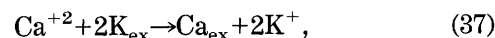
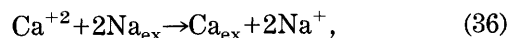
#### ION EXCHANGE IN RANEGRAS PLAIN

The ion-exchange reactions of calcium, sodium, potassium, and magnesium are quantified through the derivation of the mass transfer using the composition of a high-sulfate, high-chloride ground water in Ranegras Plain. Along the flow path from the Granite Wash Mountains to Ran 4 (fig. 21), sodium concentrations

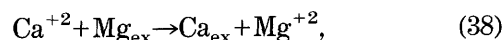
increase from 0.97 to 41.30 mmol (22 to 950 mg/L), magnesium concentrations increase from 0.6 to 3.3 mmol (15 to 80 mg/L), and potassium concentrations increase from 0.05 to 0.31 mmol (2 to 12 mg/L). The ground water at Ran 4 contains the largest sulfate concentration, 19.8 mmol (1,900 mg/L), and the largest magnesium and potassium concentrations in the basin. The reactions along the flow path can be written to the predominant species as



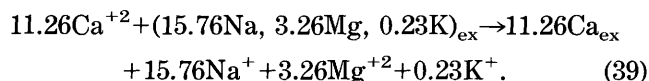
Exchange reactions that influence calcium, sodium, potassium, and magnesium concentrations in the ground water can be expressed by the following general equations:



and



and by mass balance



Thus, an exchange of 11.26 mmol, or 451 mg/L, of calcium can account for 362 of the 950 mg/L of sodium, 79 of the 80 mg/L of magnesium, and 8.9 of the 12 mg/L of potassium concentrations in solution. It is clear that the cation concentrations, when adjusted for ion exchange, and in the case of sodium, also for halite dissolution, are representative of concentrations found in dilute down-gradient waters. Also apparent is the nearly identical mass transfer of the aluminosilicates determined for other basins containing dilute waters.

An alternate reaction that may account for the large magnesium concentrations at Ran 4 is the dissolution of dolomite. The ground water is at equilibrium with respect to calcite ( $SI_{\text{cal}}=0.040$ ) and gypsum ( $SI_{\text{gyp}}=0.070$ ) and is undersaturated with respect to dolomite ( $SI_{\text{dol}}=-0.674$ ). Incongruent reactions as described by Plummer (1977) could occur where gypsum dissolution and calcite precipitation may cause dissolution of dolomite (dedolomitization). The general state of dolomite undersaturation of the ground water and the fact that dolomite was not detected during XRD analysis within the saturated zone favors the ion-exchange model. Moreover, dedolomitization would not explain the increase in potassium and sodium concentrations.

### COMPARISON OF MASS TRANSFER AMONG BASINS

A comparison of mass transfer among basins indicates that significant mass transfer of the silicates is not occurring downvalley and suggests that many basins may not have significant downvalley movement of water. Mass transfer of the silicates in the confined aquifer of lower San Pedro Valley was observed only along flow paths. Ground water originates as runoff and precipitation along the Galiuro Mountains, moves normal to the mountains to the basin axis, and is discharged by dense phreatophytes along a line sink. The narrow basins in the southeastern part containing line sinks, and at least one basin in the northwestern part, Big Sandy basin (Davidson, 1973b), do not have significant downvalley movement of water.

Small ground-water flows moving downvalley may not be limited to basins in the southeastern and northwestern parts that contain extensive linear sinks. For example, in arid McMullen Valley, where confined conditions and extensive phreatophytes are not present as in lower San Pedro Valley, a similar lack of downvalley movement is suggested by the high degree of chemical reaction from the recharge area along the mountains to the center of

the basin and by the small mass transfer of the silicates between the upper and lower parts of the valley. In fact, larger reaction coefficients were derived for the upper part than for the lower part. An explanation for the observed mass transfer may lie in the distribution of precipitation and recharge and the evapotranspiration patterns. A major hydrologic difference between the two valleys is that the lower San Pedro Valley drainage area receives greater precipitation and recharge. The greater recharge and ground-water flow cannot be discharged by underflow rapidly enough to prevent the buildup of heads, resulting in high potentiometric surface and shallow water tables which, in turn, result in the extensive linear discharge. Underflow out of a basin is controlled by the hydraulic conductivity and the cross-sectional area of the saturated sediments at the outlet. As the cross-sectional area is considerably smaller at the outlet than at midbasin, owing to typical narrowing of the basin and thinning of the sediments, shallow water levels may be present even in downvalley areas in basins that presumably receive minimal or insignificant recharge. Although basins in arid areas like McMullen Valley do not discharge ground water along their entire axis, some discharge probably occurs near the outlet.

The amount and distribution of precipitation are crucial to the annual recharge of a basin. Metzger and Loeltz (1973) determined that the total annual precipitation within the watershed of the lower Colorado River area must exceed 8 in before any recharge can occur. Precipitation below this threshold value serves only to satisfy soil-moisture deficits and evapotranspiration losses. In McMullen Valley, only the precipitation within the central parts of the Harcuvar and Harquahala Mountains may be providing recharge to the basin aquifer, as precipitation in the distal areas is marginally greater than a presumed threshold value of 8 to 10 in. Thus, the ground water, which may be recharged primarily at midvalley, moves only a short distance downvalley and discharges under shallow water-table conditions near the basin outlet during periods of high evapotranspiration. Phreatophyte growth, although not as dense as the mesquite forest in lower San Pedro Valley, may be commensurate in abundance with the discharge. Significant phreatophyte growth is present in downvalley areas of McMullen Valley, Butler Valley, Ranegras Plain, Harquahala Plain, La Posa Plain, and other west-central basins. Analogous to lower San Pedro Valley, large fluxes of water may not be moving down the entire valley and out of the basin. Thus, the chemical cycle repeats itself in the adjoining basin of lower altitude, a trend observed throughout most of the study area. The chemical data suggest that ground-water movement is not characterized by a continual increase in downvalley flow from basin to basin.



### DISTRIBUTION PATTERNS OF MASS TRANSFER

The mass transfer derived for the basins may be illustrated by two general distribution patterns—those shown by the narrow basins like lower San Pedro Valley in the southeast and those shown by the oval basins like Vekol Valley and Ranegras Plain in the south-central and western areas. The patterns are related primarily to the difference in precipitation and distribution of recharge. Two patterns of mass transfer derived through weathering of andesine and augite are shown in figure 38. The mass transfer in the basins of the southeast (figs. 38A, 38B) is characterized by an equipotential pattern that parallels the mountains. The equipotential distribution is indicative of significant recharge along the entire perimeter of the basin and corresponding discharge along the entire central drainage. The idealized pattern of the west-central basins is indicative of lesser recharge confined to, in this example, two general areas (figs. 38C, 38D).

Figures 38C and 38D show the effect of an ephemeral stream on the water chemistry in the downvalley area under shallow water-table conditions; the small mass transfer of andesine and augite shown was derived along the extreme lower reach of Bouse Wash near Bouse in Ranegras Plain. Recharge is occurring along a sandy phreatophyte-free channel under shallow ground-water conditions of about 80 ft to water. Chemical and isotope data from well (B-6-17)12dbb2 near the wash confirm recharge along the wash; a  $\delta^{13}\text{C}$  of  $-12.7\text{‰}$  and the major element chemistry are in good agreement with mountain-front recharge compositions. The deuterium content of  $-54.0\text{‰}$  of water from this narrow band of local recharge is enriched about  $15\text{‰}$  relative to ground water in the regional system, which originates near the Plomosa and Granite Wash Mountains. The enrichment in deuterium along the wash relative to the regional system is attributed to infiltration of water during summer flood events, as higher seasonal temperatures favor enrichment. Surface runoff from the mountain fronts commonly reaches the valley floors in response to high-intensity summer thunderstorms.

The distribution of stable-isotope and chemical data in Ranegras Plain validates the two fundamental principles regarding the chemical models and basin hydrology: (1) the predominance of mountain-front recharge and (2) the existence of a closed hydrochemical system. The hydrochemical system of most basins in the study area is depicted as the regional recharge being attributed to winter precipitation along the mountain fronts and the local infiltration of water being attributed to summer flow events only in areas of shallow water. Most of the water in storage originates as winter precipitation that infiltrates along mountain fronts and evolves under

closed conditions through rock-water weathering reactions, as suggested by the distribution patterns of mass transfer shown in figure 38.

### BASIN CATEGORIZATION AND INFORMATION TRANSFER

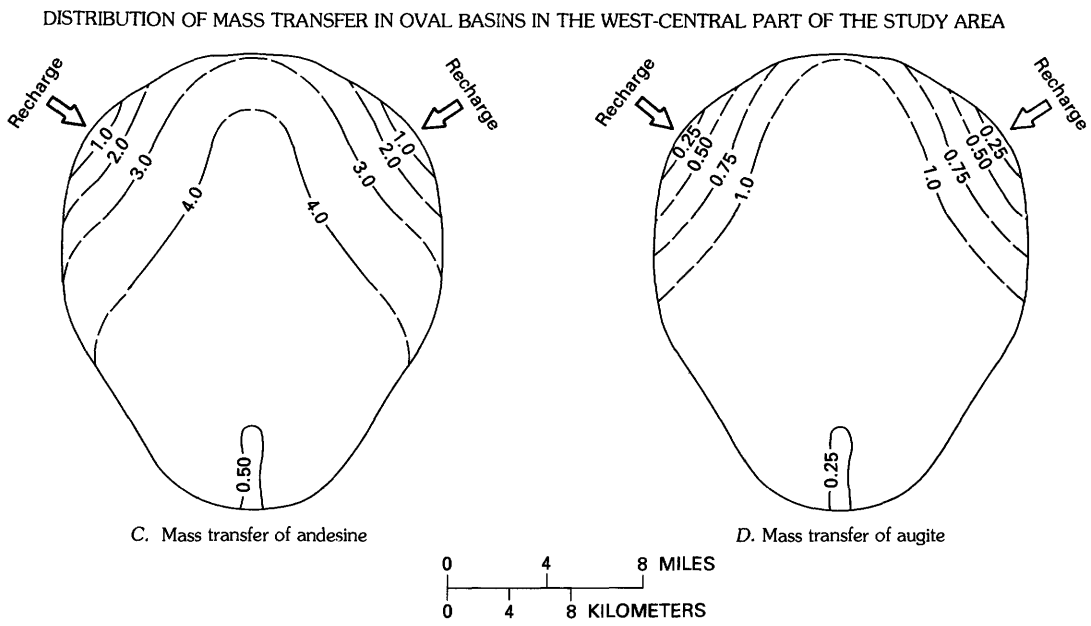
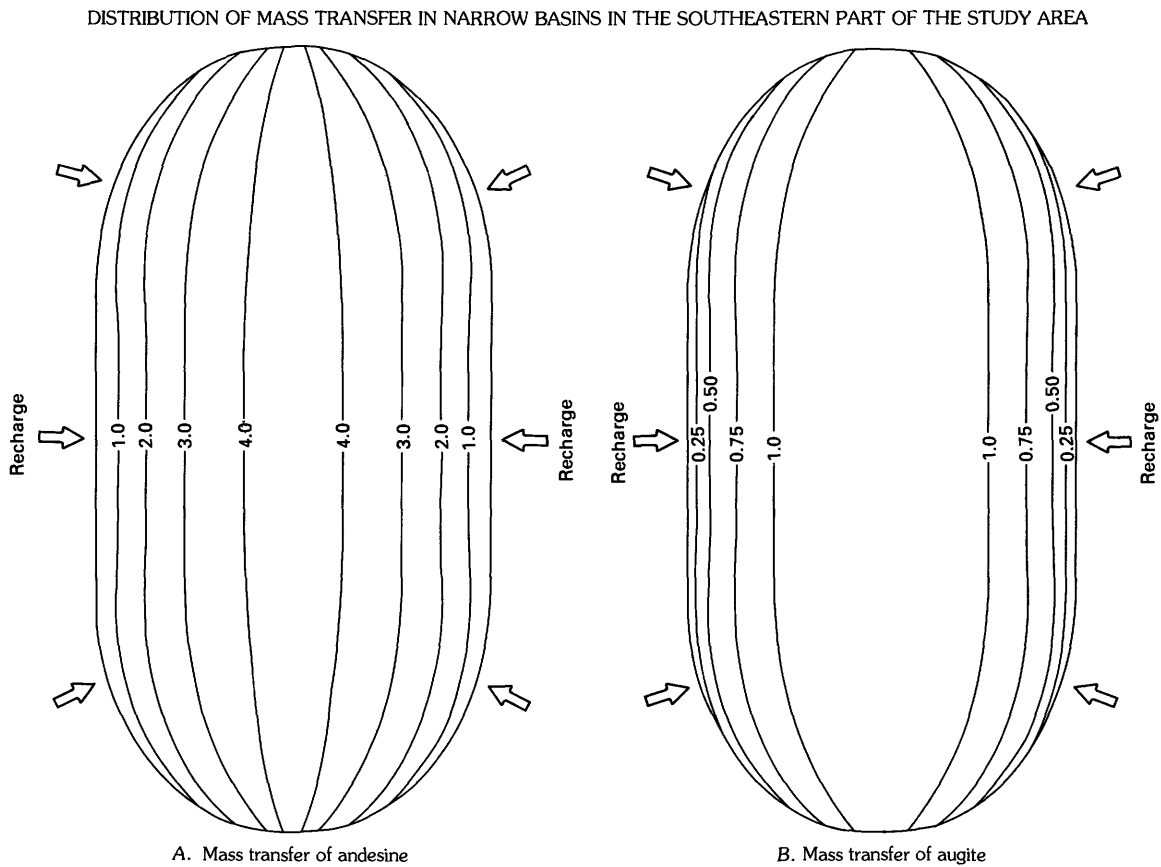
A primary goal of the geochemistry study was to develop information transfer from basins for which the geochemistry and the water quality are understood to basins for which data are inadequate and geochemical histories are complex. The information, which includes geochemical concepts, reactions, and water quality, was transferred or projected through categorization of the basins according to physiographic, geologic, and hydrologic characteristics and their effect on geochemistry. The basins in the study area were divided geochemically into two general groups on the basis of an open or closed chemical evolution. Geochemistry and water quality can be reasonably predicted for other basins by evaluating the geologic and hydrologic parameters of these basins and using the assumptions and model results pertinent to each group.

#### BASIN CATEGORIZATION

The basins were categorized as open basins, basins that contain open evolutionary systems, in the eastern part of the study area, and closed basins, basins that contain closed evolutionary systems, in the west-central part. (See section entitled "Evolution of the Ground Water in Selected Basins.") The eastern basins have bordering mountains of high altitude that provide greater precipitation and greater recharge potential, and some have a coarse-grained upper basin-fill unit that allows infiltration and percolation of runoff along the valley floor. The west-central basins receive less precipitation and thus less recharge, and many have a fine-grained unit overlying the aquifer, factors that favor a closed system. Exceptions are basins in the western part that are dominated by the Colorado River and parts of basins in the southeast that contain the confined aquifers.

#### OPEN BASINS

The Willcox and Douglas basins, upper San Pedro Valley, and the Tucson basin in the upper Santa Cruz area are categorized as open basins. The Tucson basin, one of the largest basins in the study area, is a good example of an eastern basin. The open system is a result of the high annual precipitation in the Santa Catalina (greater than 35 in), Tanque Verde (greater than 25 in), and Rincon (greater than 30 in) Mountains bordering the



EXPLANATION

—1.0— LINE OF EQUAL MASS TRANSFER—Interval, in millimoles per 1,000 grams of water, is variable. Line dashed where extrapolated

FIGURE 38.—Idealized distribution of mass transfer.

northern and eastern parts of the basin and the numerous streams that drain these mountains. Major streams that traverse the basin floor are the Santa Cruz River, Pantano and Aqua Caliente Washes, Canada del Oro, and Tanque Verde, Rillito, Big, Sabino, and Rincon Creeks. Most of the estimated annual recharge to the aquifer of 100,000 acre-ft is supplied by infiltration along these streams (Davidson, 1973a). The shallow depths to water of 25 to 250 ft (Davidson, 1973a) throughout the basin and the generally permeable deposits of the upper basin fill (Fort Lowell Formation of Pleistocene age) favor infiltration and recharge in many other canyons and stream channels in the basin.

The shallow water-table aquifers overlying the confined aquifers in the eastern part also are open systems. These open systems include the saturated stream sediments along the San Pedro, Gila, and Salt Rivers and San Simon Wash. Open systems also occur in the shallow stream aquifers in the intermontane basins of the Central highlands water province. Altar and Avra Valleys also are open or partially open basins and are in a transition zone between the open and closed systems, primarily because of the westward trend of decreasing precipitation. Open systems may occur in large parts of Altar and Avra Valleys owing to the presence of a moderately coarse grained upper basin-fill unit. Closed conditions may exist in many basins near the mountains depending on the depth to water and, locally, on the thickness, vertical hydraulic conductivity, and areal extent of any fine-grained unit overlying the aquifer.

#### CLOSED BASINS

Most of the basins in the western and central parts of the study area are categorized as closed; the eastern basins that contain the confined aquifers also are considered closed basins. Through examination of water-level data, water chemistry, geology, or stratigraphy, closed systems were indicated in Vekol, McMullen, Butler, Rainbow, and Hualapai Valleys, Harquahala and La Posa Plains, the Bullard Wash area, and the Big Sandy basin in the west-central area. A large part of the Big Sandy basin may contain an extensive aquifer underlying the shallow water-table aquifer along the Big Sandy River. Because of an abundance of shallow ground water along the river and lack of development elsewhere, data to define the underlying aquifer were not available throughout the rest of the basin. In the eastern part of the area, the confined aquifers in lower San Pedro, San Simon, and San Bernardino Valleys, the Benson area, and the Safford basin are also categorized as closed systems.

Closed systems occur in East and West Salt River Valleys in areas away from the river where depths to

water exceed approximately 200 ft and are not influenced by irrigation return flow. A closed system is also found in a large part of Verde Valley. Closed conditions occur in parts of Little Chino Valley and of the adjacent Agua Fria River area that are not influenced by streams of the area. The analysis of available data for the Maricopa-Stanfield and Eloy areas and many of the smaller nearby basins on the Papago Indian Reservation indicates that most of the ground water probably evolves under closed conditions. On the basis of few data, open and closed conditions apparently occur in parts of Sacramento and Detrital Valleys. Virtually no data are available for the Castle Dome and Palomas Plains, King and Mohawk Valleys, the San Cristobal Wash and Growler Wash areas, and Lechuguilla Desert in the extreme southwestern part of the study area, but owing to the sparse precipitation in the area, ground water may evolve under predominantly closed conditions.

#### PROJECTION OF GROUND-WATER CHEMISTRY

##### OPEN SYSTEMS

The ground water evolving under open conditions is characterized by large and variable concentrations of calcium, magnesium, and bicarbonate ions. In dilute waters, the concentrations of these ions are the major differences in chemistry between the open and closed systems. The chemical data available for the Tucson basin show such variability and suggest that the ground water evolves under open conditions throughout much of the basin. Variable concentrations may be the result of dissolution of calcite or dolomite under shallow water-table conditions, as described by equation 26. Concentrations of these elements would be determined mainly by a reservoir of soil  $\text{CO}_2$  and the availability of calcite or dolomite in the soil or basin fill.

Upward leakage from the confined aquifers may be an additional factor affecting the water chemistry of the overlying shallow unconfined aquifers. In the unconfined aquifers along the rivers in lower San Pedro Valley and in the Safford basin, for example, the water chemistry of all dissolved species is variable. Some of the variability, particularly of sulfate and chloride, could be caused by upward leakage through the gypsiferous deposits known to be present. Highly variable fluoride concentrations unique to the unconfined aquifers that overlie the confined aquifers may also be a result of upward leakage (Robertson and Garrett, 1988). The presence of halite or gypsum, although much less common in the upper unit or stream alluvium, would also cause some variability. Because of the inherent problem in open systems of the mixing of waters having different compositions, a general process was not developed for describing reactions

quantitatively and for projecting water chemistry. However, if ground water in an open system is anticipated to be high in dissolved solids, techniques described in the next section may make it possible to project water chemistry. Projections are possible because the differences in the chemical compositions of the water evolved under the two processes decrease as the salinity increases and because the salinity is caused primarily by dissolution of halite and gypsum and their mediation of other ions.

#### CLOSED SYSTEMS

The modeling used in conjunction with the analytical techniques developed during this study has proved valuable in projecting water chemistry and geochemical trends in basins with closed systems. The concentrations of the major dissolved species can be estimated with reliability, and occurrences of some trace elements can be projected. Average values for major ions in downgradient waters, based on 21 analyses from the Big Sandy basin, Harquahala Plain, San Simon Wash area, and Little Chino, lower San Pedro, Butler, McMullen, West Salt River, Hualapai, Paradise, and Altar Valleys, where closed conditions exist, are shown in table 29. If ground water in any basin evolves in a closed system and is low in dissolved solids (less than 50 mg/L of sulfate and chloride), the concentrations of the major ions should fall within the range indicated by the analyses. If the ground water contains larger dissolved-solids concentrations, the water will have the composition of these dilute waters plus the additional sulfate and chloride concentrations, plus sodium concentrations equal to molar increases of chloride and any exchange of calcium for sodium provided by the dissolution of gypsum. Calcium concentrations would be equal to those in table 29 plus the increase in molar concentrations in sulfate, minus any exchange of calcium for sodium. The nature of the ion-exchange mechanism and the extent of exchange of all cations in waters of differing salinity are not clear but can be empirically estimated for sodium by assigning 40

percent of the calcium increase supplied by the gypsum increase to ion exchange. A twofold or threefold increase in magnesium and potassium concentrations may occur if the ground water contains concentrations of sulfate in excess of 500 mg/L. These concentrations may increase severalfold if sulfate concentrations increase to more than 1,000 mg/L. The composition of the ground water can be estimated after an analysis for chloride and sulfate, which can be done quickly and accurately in the field.

In an area where a water sample is not available for analysis, the chemical composition of the ground water can nonetheless be estimated from basin-fill material. Techniques for analyzing the solid species—well cuttings or drill core—developed during the study may also be used for projection of ground-water chemistry. The analysis consists of leaching small amounts (2–4 grams) of the material in distilled water and analyzing the leachate for chloride, sulfate, nitrate, and fluoride by ion chromatography. The concentrations of chloride, sulfate, and nitrate in the leachate closely approximate actual concentrations of these ions in the ground water from the completed wells. Analyses of well-cuttings leachate and of ground-water compositions from Vekol Valley and the Bosque basin (in Gila Bend Plain) are shown in table 30 and illustrate the degree of confidence of the predictive technique. Thus, most major ion concentrations can be approximated without the expense of large-diameter boreholes and installation of casing and pumping equipment. Water compositions can be estimated by analyses of samples from small-diameter drill core or of material that is already stored in repositories. This predictive technique is a potentially powerful tool for evaluation of water quality and geochemistry in undeveloped areas in the southwest as well as in the study area.

Occurrences of  $\text{Cr}^{+6}$  and larger concentrations of fluoride can be expected in the arid west-central basins. Closed systems favor high pH values and the removal of solute calcium, factors that may produce large fluoride concentrations. The high pH values and the long residence time of these waters also may cause large hexavalent chromium concentrations. The few data available in the western part of the study area support this projection, as the ground water contains noticeably large fluoride and hexavalent chromium concentrations.

Hexavalent chromium, however, is conspicuously absent in the southwestern part of the study area near Yuma, which is the most arid part. The absence probably is due to the distribution of the sampling points. A large part of the area consists of bombing and gunnery ranges or other military installations, and little development has occurred. Most samples were taken from wells in the Colorado River flood plain or along the Gila River between Gila Bend and Yuma and were from shallow,

TABLE 29.—Average major ion concentrations in dilute downgradient waters

	Millimoles per liter		Milligrams per liter	
	Mean	Standard deviation	Mean	Standard deviation
$\text{Ca}^{+2}$ .....	0.215	0.11	8.6	4.4
$\text{Mg}^{+2}$ .....	.084	.07	2.0	1.7
$\text{Na}^{+}$ .....	3.782	1.15	87	28
$\text{K}^{+}$ .....	.047	.02	1.8	.8
$\text{Cl}^{-}$ .....	.929	.53	33	19
$\text{SO}_4^{-2}$ .....	.387	.23	37	22
$\text{HCO}_3^{-}$ .....	2.387	.47	146	29
$\text{SiO}_2$ .....	.443	.17	27	10

TABLE 30.—*Analyses of well-cuttings leachate for chloride, sulfate, nitrate, and fluoride from wells in Vekol Valley and the Bosque basin (Gila Bend Plain)*

[In parts per million\* except as indicated. Analyses by Center for Meteorite Studies, Arizona State University]

Depth of sample, in feet below land surface	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	NO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
(D-9-1)13bbd (Vekol Valley)				
370.....	103	62	<30	24
470.....	65	54	<30	7
730.....	54	44	<30	9
1,410.....	51	55	<30	6
1,610.....	69	71	<30	7
1,910.....	97	57	<49	7
2,100.....	94	104	36	8
Average .....	76	62	<42	9.25
Analysis**....	78	95	37.4	0.5
(C-6-3)2acd (Bosque basin)				
320.....	166	177	<30	9
640.....	278	149	<30	13
840.....	117	45	<30	4
1,040.....	232	131	<30	9
1,350.....	250	110	66	6
1,620.....	188	60	<30	4
1,950.....	280	136	<30	7
2,120.....	94	72	<30	4
Average .....	201	110	<66	7
Analysis**....	170	120	31.6	0.3

\*Reported on dried sample basis.

\*\*Analysis of ground water from completed well.

open-system aquifers. It is quite probable that if wells are drilled away from the rivers where depths to water exceed 150 ft, the presence of chromium in the ground water will be detected.

## SUMMARY

Ground water in the alluvial basins of the Southwestern United States has been the subject of geochemical and water-quality investigations as part of the Southwest Alluvial Basins Regional Aquifer-System Analysis Program. The study area encompasses about 82,000 mi<sup>2</sup> in the Basin and Range physiographic province in Arizona and small parts of adjacent States. The principal landforms of the area are a series of north- to northwest-trending mountains and basins, which were formed by large-scale normal faulting during the Basin and Range disturbance 14 to 6 million years ago. The mountains in the area consist of Precambrian and Tertiary metamorphic and intrusive rocks, Paleozoic sedimentary rocks, Mesozoic igneous and sedimentary rocks, and Tertiary volcanic and sedimentary rocks. The basins contain alluvial deposits of late Cenozoic age that attain thicknesses of many thousands of feet. The basin fill was deposited by

local drainage processes, as indicated by the clast type, the basinward increase in fine-grained materials, and the proximity of the finest grained and thickest deposits to the basin center. The basin deposits are divided into three units—the lower basin fill, the upper basin fill, and the stream alluvium—on the basis of source, particle size, and composition. The lower basin fill generally is highly consolidated and deformed and contains the finest grained deposits. Evaporites, where present, occur predominantly in this unit. The upper basin fill was deposited near the end of the Basin and Range disturbance and is coarser grained and less cemented, deformed, tilted, or faulted than the lower unit. The sediments of the stream alluvium generally are less than 100 ft thick and are found along rivers and streams.

The mountains that surround the basins have little permeability and form ground-water divides that separate the study area into 72 basins or individual alluvial aquifers. These aquifers join together in a dendritic pattern to form the regional aquifer system. Ground water is recharged to the aquifers by infiltration of precipitation and runoff along the mountain fronts, by infiltration along streams, and by underflow from adjacent basins of higher altitude. The chemical and isotope data indicate that in most basins the major recharge occurs along the mountain fronts. Ground-water discharge from basins occurs through evapotranspiration, ground-water underflow, pumping, and discharge to streams. Ground water generally is under unconfined conditions, but confined conditions are common throughout the eastern part of the study area where areally extensive fine-grained facies of the basin fill and sufficient recharge occur.

X-ray diffraction analyses of the less than 62-μm fraction of the basin fill show that plagioclase, potassium feldspar, calcite, quartz, muscovite, and smectite are the most common minerals. Dolomite was detected in the unsaturated zone of several basins but not in the saturated zone. Montmorillonite, a magnesium dioctahedral smectite, is the dominant clay in the less than 2-μm fraction, but trace to small amounts of kaolinite and muscovite are present. Chlorite and vermiculite are not present. Montmorillonite is the most stable phase within the basin fill, as indicated by its abundance and the saturation state of the ground water. Variations in precipitation, altitude, and vegetation among the basins apparently have little influence on the type of clay formed. The clay mineralogy of the soil zone is similar to that of the basin fill; montmorillonite is the dominant clay, but mica and kaolinite may be more abundant.

The chemical quality of the ground water is suitable for most purposes but is not without problems. Most basins contain ground water with less than 1,000 mg/L dissolved-solids concentrations, but ground water in

some basins contains concentrations in excess of 3,000 mg/L and can be classified as hard to very hard. All ground water sampled contained dissolved-oxygen concentrations near 70 percent or more of saturation. Owing primarily to the oxidizing environment and the abundance of trace elements in the basin fill, the ground water in several basins contains large concentrations of trace elements that exceed Federal and State maximum contaminant levels or toxicity levels for plants. The constituents of fluoride, chromium, arsenic, boron, and nitrate, in particular, present environmental problems in several basins.

The occurrence of fluoride in the ground water may be related to mineral-equilibrium and sorption or desorption reactions. The mineral fluorite apparently is a control of fluoride in water that contains concentrations greater than about 5 mg/L. Smaller concentrations seem to be controlled by pH-dependent exchange reactions. Availability of the fluoride in the rocks may be an additional control; large fluoride concentrations are correlated with acidic and intermediate volcanic rocks and their weathering products. Hexavalent chromium is a naturally occurring constituent in ground water throughout much of central and western Arizona. The observed concentrations are a result of oxidation of  $\text{Cr}^{+3}$  in the basin fill, apparently under thermodynamic-equilibrium conditions. The larger concentrations tend to be associated with intermediate volcanic rocks. The weathering of sulfide and arsenide mineral deposits probably is the primary source of arsenic. Mineralogic controls appear to have little or no effect on arsenic solubility in the oxygenated environment in which arsenic occurs as the arsenate ion. A major control of arsenic occurrence and removal is the coprecipitation or adsorption of the arsenate ion on ferric oxide or ferric oxyhydroxide surfaces. Boron concentrations are larger in the western basins and may be a function of reworking and concentrating of boron in the soil. The largest concentrations are related to playa or evaporite deposits where the soluble borate compounds tend to be concentrated. The geochemical behavior of nitrogen is parallel to that of boron. Nitrate, the most stable species of nitrogen in the ground water, is highly soluble and also tends to be enriched in the basin centers. Large nitrate concentrations have multiple sources. Selenium is geochemically similar to arsenic, and, like arsenic, concentrations may be controlled by sorption-desorption reactions on ferric oxide or ferric oxyhydroxide surfaces. The concentrations of barium in the ground water are controlled solely by the solubility of the mineral barite and generally do not exceed the maximum contaminant level of 1.0 mg/L. The weathering of alkali feldspars is the major source of barium in the ground water.

Geochemical models were developed to identify reactions and mass transfer responsible for the evolution of

the ground water. On the basis of the mineralogy and chemistry of the rocks of the surrounding mountains and of the basin fill, two chemical models—a mafic model and a felsic model—were developed to define reactions. Two distinct hydrochemical processes were identified: reactions of meteoric water with minerals and gases in the recharge areas, and reactions of the ground water as it moves downgradient within the aquifer. Major reactions controlling the recharge chemistry are the weathering of feldspars and ferromagnesian minerals, dissolution of carbonate minerals, and formation of montmorillonite and iron oxyhydroxides in an acid environment. Major reactions controlling the chemistry downgradient are the weathering of plagioclase, formation of montmorillonite, precipitation of calcite, and possibly of silica, and, in some basins, ion exchange of calcium for sodium, potassium, and magnesium. Geochemical models were developed for several basins to determine geologic, climatic, and physiographic effects on ground-water chemistry. Relatively few phases are required to account for the chemical evolution of the ground water; for each basin, 14 phases—12 mineral and 2 gas—accounted for the ground-water evolution and changes in water chemistry.

The high partial pressure of soil  $\text{CO}_2$  and the high reaction rates of the silicates in the recharge waters suggest that carbonic acid supplies the impetus in the weathering process and is considerably more important than the residence time of the ground water. The transport of  $\text{CO}_2(\text{g})$  through the unsaturated zone has not been defined but is postulated to occur via deep percolation during recharge. Reactions in the unsaturated zone appear to be highly influential in determining the composition of the ground water. Compositions of some ground water from different geologic terranes appear similar to or unrelated to obvious source rocks. Reasons for these similarities or anomalies are unclear; possible explanations are inconsistencies between the mineralogy of the basin fill and that of the mountains and reactions mediated by climate and precipitation in the unsaturated zone that may be obscuring or altering initial compositions.

The basins were divided geochemically into two categories, closed and open systems. In closed systems the aqueous chemistry is determined solely by reactions of the initial recharge water with minerals and gases as it moves downgradient. Conversely, in open systems the aquifer chemistry is controlled or influenced by gases or water that enter the system after the initial recharge.

In closed systems, the reactions and associated mass transfer were successfully defined along flow paths and were found to be consistent within and among basins. In open systems, probable reactions were identified but the mass transfer along the flow path could not be defined, as the chemistry is influenced by additional recharge. Reac-

tions in the unsaturated zone seem to play a larger role in open systems than in closed systems. The decisive factors in determining whether reactions occur in an open or closed system are the annual precipitation that falls within the basin drainage area and the presence or absence of fine-grained units. Basins in areas of higher precipitation in the eastern part of the study area and those along the Colorado River were categorized as open systems. Most basins in the central and western parts were categorized as closed systems, as were the confined aquifers in basins in the east. The closed systems were supported by stable and radiogenic isotope data and by the transferability and consistency of reactions from the confined aquifers of the eastern basins to the generally unconfined aquifers of the western basins. The consistency of the mass transfer of the silicates among basins clearly indicates that the major reactions have been identified.

The basins adjoining the Colorado River are unique among other basins in the region because they were formed by and are hydrologically dominated by a major river. Most of the ground water in basins along the river originated as infiltration of river water or, before construction of the dams, as overbank flow during spring floods. Ground water that originates from the river may extend several miles beyond the flood plain into the piedmont areas. The  $\delta D$  and  $\delta^{18}O$  of the ground water in these basins plot along a line having a slope of 5, indicating enrichment of the heavier isotopes through evaporation. The initial deuterium content of the river water of about  $-120\text{‰}$  is indicative of that of the precipitation in central Colorado. Reactions proposed in the literature to account for the chemical evolution of the ground water along the river, namely concentration through evapotranspiration, sulfate reduction, and precipitation of carbonates, are not realistic. The chemical and isotope data indicate that increases in salinity and changes in sulfate to chloride ratios generally are not a function of sulfate reduction or evapotranspiration. Reactions were developed that show weathering of silicates and the dissolution of gypsum, halite, and calcite are considerably more realistic in accounting for chemical evolution and increased salinity of the ground water.

Ion exchange is not a significant reaction in basins that contain ground waters having low dissolved-solids content. However, ion exchange of calcium for sodium, potassium, and magnesium is a significant reaction in basins that contain large concentrations of dissolved solids and sulfate. The uptake and release of potassium through exchange reactions is the most important control of solute potassium. In the gypsiferous waters of several basins, ion exchange of calcium for magnesium is the major cause of large concentrations of magnesium in the ground water.

The information obtained from the modeling and the analytical techniques developed during this study can be used to project ground-water chemistry throughout most of the area. Water compositions for the major ions can be estimated from a simple field analysis of the water for sulfate and chloride or from an analysis of the basin-fill material for these two ions. This predictive technique is a potentially powerful tool for evaluation of the water quality and the geochemistry in undeveloped areas in the Southwest.

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