GEOCHEMISTRY OF GROUND WATER IN THE SACRAMENTO VALLEY, CALIFORNIA

REGIONAL AQUIFER-SYSTEM ANALYSIS

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Geochemistry of Ground Water in the Sacramento Valley, California

By LAURENCE C. HULL

CENTRAL VALLEY OF CALIFORNIA RASA PROJECT

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CONVERSION FACTORS

Factors for converting inch-pound units to the International System (SI) of units are given below:

Multiply	*By*	*To obtain*
acres	0.004047	km^2 (square kilometers)
acre-ft (acre-feet)	0.001233	hm^3 (cubic hectometers)
ft (feet)	0.3048	m (meters)
mi (miles)	1.609	km (kilometers)
mi^2 (square miles)	2.590	km^2 (square kilometers)

Degrees Fahrenheit are converted to degrees Celsius by using the formula: °C=(°F-32)/1.8

Additional abbreviations:

µg/L	(micrograms per liter)
mm	(millimeters)
mg/L	(milligrams per liter)
(mg/L)/yr	(milligrams per liter per year)

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 mean sea level. NGVD of 1929 is sometimes referred to as sea level in this report.

GEOCHEMISTRY OF GROUND WATER IN THE SACRAMENTO VALLEY, CALIFORNIA

By LAURENCE C. HULL

ABSTRACT

A geochemical investigation was done to evaluate temporal changes in water quality and to determine the processes that control water chemistry in shallow ground water of the Sacramento Valley, California. A total of 671 chemical analyses from 651 wells were used to study the processes controlling water chemistry. Temporal variations in dissolved-solids and nitrate concentrations were studied in 140 and 62 wells, respectively, having multiple observations with time.

The Sacramento Valley can be divided into six hydrochemical facies having distinctive chemical compositions. Waters from the Tuscan volcanic rocks and Victor Plain facies, along the eastern margin, have lower concentrations of dissolved solids and higher concentrations of silica than the waters from other areas of the Sacramento Valley. Ground waters in the basin hydrochemical facies (Butte Basin and Sutter Basin) along the valley axis are higher in iron, manganese, arsenic, and potassium. West side facies, the north alluvial fans and south alluvial fans, are low in silica. The south alluvial fans facies is higher in dissolved solids and has very high boron concentrations.

Significant increases have occurred in dissolved-solids and nitrate concentrations since the mid-1950's. Dissolved solids increased in five of the six hydrochemical facies, with rates ranging from 0.95 milligrams per liter per year in the Tuscan volcanic rocks facies to 4.75 milligrams per liter per year in the south alluvial fans facies. Nitrate-nitrogen did not significantly increase in the Tuscan volcanic rocks, Butte Basin, or Sutter Basin hydrochemical facies. Rates of increase of 0.036, 0.036, and 0.099 milligrams per liter per year occurred in the Victor Plain, south alluvial fans, and north alluvial fans, respectively.

Two processes control over 50 percent of the spatial variation in ground-water chemistry. Thirty-six percent of the variation in the data is explained by the effects of recharge water chemistry on the chemistry of ground water. Low dissolved solids and high silica from east-side recharge produces fairly uniform conditions in east-side ground waters. Recharge from the northwest is intermediate in dissolved solids and silica. Southwest recharge is high in dissolved solids, boron, and fluoride. High boron concentrations in the ground water originate in thermal springs in the Coast Ranges. A second important process consists of reactions occurring in the fine-grained sediments of the flood basin in the central part of the Sacramento Valley. Reducing conditions here produce higher concentrations of manganese, iron, and arsenic. Nitrate concentrations are low, probably reflecting denitrification reactions.

Precipitation and dissolution of aluminosilicates appear to control the relation between silica and aluminum in parts of the valley. Silica and aluminum in ground waters of the Sutter Basin hydrochemical facies show parallel behavior and have a ratio of 3 to 1. In the Tuscan volcanic rocks facies silica and aluminum are inversely related and are controlled by the solubility of halloysite. The clay minerals halloysite and illite were identified in the sediments. The clay mineral predicted to be the most stable in equilibrium with valley ground water is montmorillonite. Halloysite represents an intermediate step in the weathering of primary minerals to more stable secondary phases.

INTRODUCTION

GEOGRAPHY

The Sacramento Valley comprises the northern third of the Central Valley of California in the north-central part of the State (fig. 1). It is a sedimentary basin bounded by mountains to the east (Sierra Nevada), northeast (Cascade Range), and west (Coast Ranges). To the south, the valley merges with the delta of the Sacramento and San Joaquin Rivers. The area lies between 38°30′ and 40°15′ N. latitude, and 121°15′ and 122°30′ W. longitude. The valley covers about 4,400 square miles, is 150 miles in length from Red Bluff to the delta, and ranges in width from about 8 miles at Red Bluff to about 50 miles near the southern end. The topography consists of generally flat plains, with low dissected hills near the margins. The elevation of the valley at the southern end is near sea level, increasing northward and reaching 300 feet above sea level near Red Bluff. The relatively flat topography of the valley is interrupted near the center, where a volcanic neck of late Tertiary age, Sutter Buttes, rises 2,100 feet above the valley floor.

The Sacramento River enters the valley from the north and flows along the entire length of the valley before entering the delta region to the south. The Feather River is the only other principal stream that flows through the valley. The Sacramento and Feather Rivers are fed by tributaries draining the surrounding mountain areas. From the Sierra Nevada come the American, Bear, Yuba, and Feather Rivers. The Cascade Range is drained primarily by Big Chico, Butte, Mill, and Deer Creeks in the area adjacent to the Sacramento Valley. The streams entering the valley from the west rise in the Coast Ranges and are much smaller than the streams from the east. Thomes, Stony, Cache, and Putah Creeks are the only sizable streams entering

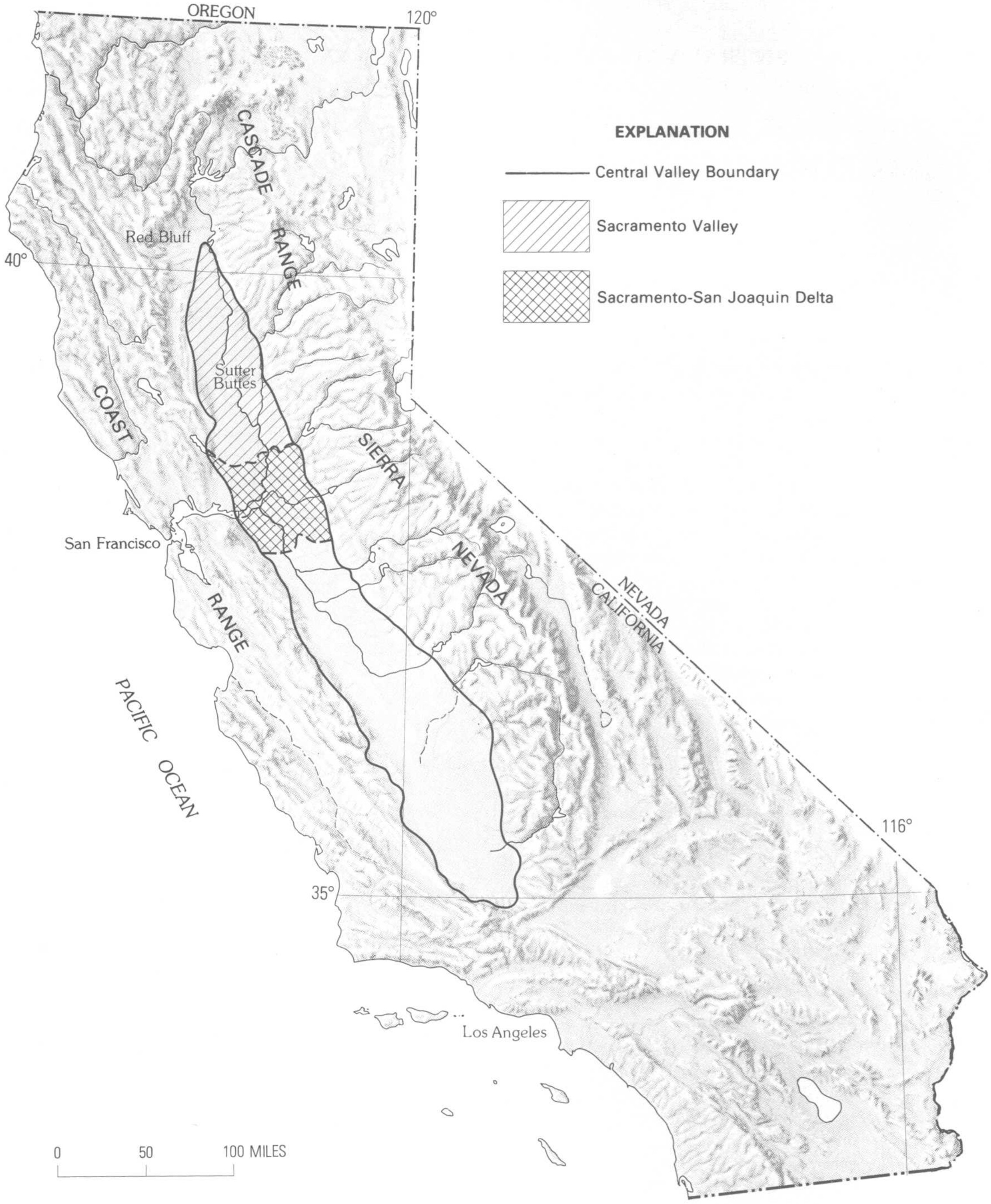

FIGURE 1.—Location map showing Sacramento Valley of California.

the west side of the valley. (See pl. *1B* for stream locations.)

Little precipitation falls in the valley during the summer growing season, and irrigation is necessary to support extensive agricultural development. Early irrigated farming began in the mid-1800's as the gold miners moving to California created a demand for foodstuffs. Development of irrigation was slow, however, until the drought of 1864 stimulated the construction of new irrigation projects. During both world wars, heavy demand for agricultural products spurred periods of rapid development. Ground water has always lagged behind surface water as a source of irrigation water, amounting to only about 10 percent of the total use in the late 1910's. Since the late 1950's, however, the use of ground water has been increasing, and in 1970, it accounted for about 40 percent of all irrigation water used in the Sacramento Valley.

PURPOSE AND SCOPE

The U.S. Geological Survey began a series of hydrologic investigations—the regional aquifer systems analysis (RASA) program—to aid effective management of the Nation's ground-water resources by providing information on the hydrology and geochemistry of regional aquifer systems (Bennett, 1979). The Central Valley aquifer project, covering the Central Valley of California, is one of 29 such projects throughout the country and was started because of the long history of ground-water development and the importance of the area's agricultural production to the national economy (Bertoldi, 1979). Specific water-quality information needed for effective management in the future includes (1) the general inorganic chemical character of water from aquifers currently in use, (2) delineation of areas where degradation is occurring and where degradation may occur in the future, (3) the changes that have occurred in ground-water quality with time, and (4) the processes that control ground-water chemistry. This report evaluates temporal changes and geochemical processes as they influence the chemical quality of shallow ground water in the Sacramento Valley, the northern third of California's Central Valley. A companion report (Fogelman, 1983) deals with spatial variations in the chemical character of ground water and the delineation of areas of potential water-quality problems for this same study region.

DATA COMPILATION

Collection of additional water-quality samples was unnecessary because of the extensive data base of the U.S. Geological Survey and California Department of Water Resources. Chemical analyses from 653 wells throughout the Sacramento Valley sampled by the Geological Survey between 1974 and 1976 were already in the Survey's water-quality file (Fogelman, 1975, 1976; Fogelman and Rockwell, 1977). From the unpublished files of the California Department of Water Resources, an additional 2,136 analyses from 281 wells were added to the water-quality file. During the summer of 1979, 63 additional samples were collected by the Geological Survey in Yolo County to extend coverage into an area where high boron concentrations suggested a need for water-quality evaluation. All wells from which chemical analyses were used in this study have driller's logs on file with the California Department of Water Resources. Thus, reasonably reliable information is available about depths and perforated intervals for these wells. Some of the samples represented multiple observations over time from single wells, and these were used for the temporal studies. Samples for the period 1974–79 were examined, and complete analyses with less than 5 percent error in the electrical balance between cations and anions were used to study the spatial variation in the valley. These latter data consisted of 671 analyses from 651 wells.

Manipulation of data files and the statistical analyses used in this report were accomplished using the Statistical Analysis System (SAS)[1] programs on the U.S. Geological Survey's Reston computer system.

WELL-NUMBERING SYSTEM

Wells are identified according to their location in the rectangular system used for the subdivision of public lands. The identification consists of the township number, north or south; the range number, east or west; and the section number. A section is further divided into sixteen 40-acre tracts lettered consecutively (except I and O), beginning with A in the northeast corner of the section and progressing in a sinusoidal manner to R in the southeast corner. Within the 40-acre tract, wells are sequentially numbered in the order they are inventoried. The final letter refers to the base line and meridian relative to which the townships and ranges are numbered. For the Sacramento Valley, this is the Mount Diablo base line and meridian (M). Figure 2 shows how the well number 11N/02E–23N01M is derived.

ACKNOWLEDGMENTS

The California Department of Water Resources has cooperated with the U.S. Geological Survey in past studies during which much of the data analyzed in this report were collected. The Department also provided additional unpublished chemical-quality data from their files. The author would like to thank J. R. Slack of the Geological Survey for his helpful suggestions on trend analysis. The cooperation of the residents of the Central Valley who have permitted the Geological Survey to collect water samples from their wells is also appreciated.

DESCRIPTION OF THE STUDY AREA

GEOLOGY AND GEOMORPHOLOGY

The Geology and geomorphology of the Sacramento Valley have been covered in detail by Olmsted and Davis (1961), the California Division of Mines and Geol-

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[1] Use of trade names does not imply endorsement and is used for information only.

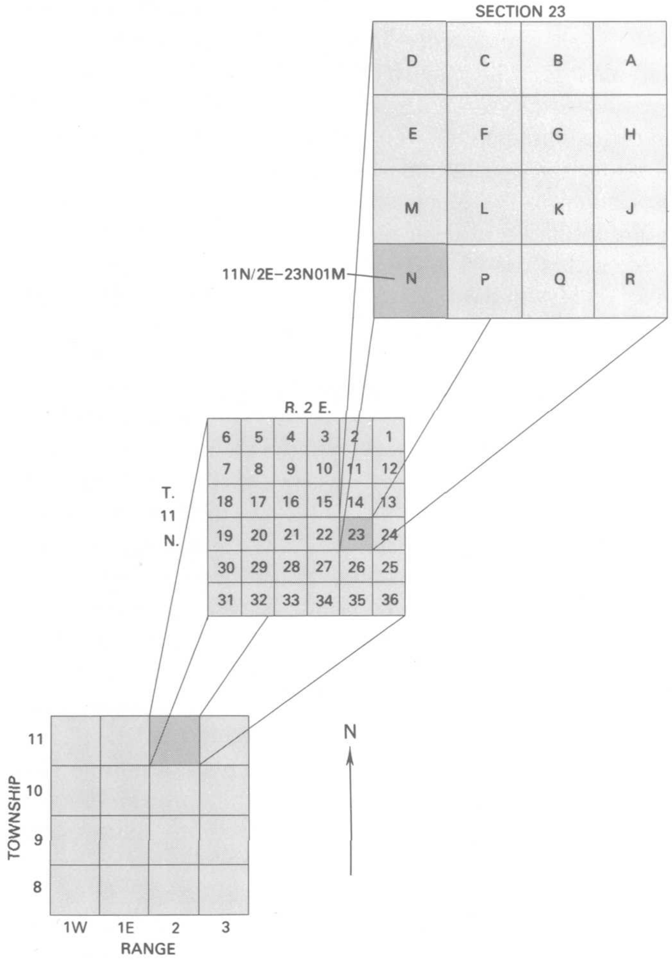

FIGURE 2.—Well-numbering system.

ogy (1966), and the California Department of Water Resources (1978a). Detailed maps and complete descriptions of the geology can be found in these publications. In this section, the geology and geomorphology are only briefly reviewed, with particular attention given to water-bearing characteristics and importance for water quality.

GEOLOGIC SYNOPSIS

The Sacramento Valley is an elongated structural trough trending to the northwest through central California. The trough is filled with a thick accumulation of sediments, perhaps as much as 50,000 feet in the deepest parts. Deposition has been occurring since early in the Cretaceous Period, with the bulk of the deposition occurring in a marine environment. A maximum of only 3,000 feet of continental deposits has been laid down as a veneer over the marine sediments. During early Tertiary time, the Cretaceous sediments west of the valley were folded and uplifted, forming the Coast Ranges and isolating the Sacramento Valley from the ocean to the west.

Early- and middle-Tertiary sedimentation was primarily confined to the southern and eastern parts of the valley, with only those sediments adjacent to the Sierra Nevada being continental deposits. During late Tertiary time, continental deposits were laid down throughout the valley, and deposition continued into Quaternary time. These continental deposits include the Tehama, Tuscan, Laguna, and Mehrten Formations and form some of the most important aquifers in the valley. Also, near the end of the Tertiary Period, andesitic lava was extruded through the older marine sediments to form Sutter Buttes, a prominent volcanic neck in the middle of the Sacramento Valley.

During Pleistocene time, continental deposition continued throughout the valley. Alluvial fans and plains developed from sediments eroded from the Sierra Nevada to the east and the Coast Ranges to the west. Continued action of rivers flowing through the valley produced alluvial channel deposits and natural levees along the axis of the valley and produced flood basins adjacent to the rivers.

GEOMORPHIC UNITS

The Sacramento Valley is generally characterized by alluvial plains and fans bounded by rugged mountains. The geomorphic units described by Olmsted and Davis (1961) are (1) Sierra Nevada, (2) Coast Ranges, (3) Cascade Range, (4) low hills and dissected uplands, (5) alluvial plains and fans, (6) flood basins, (7) stream channels and natural levees, and (8) Sutter Buttes. In this section, the location and extent of the geomorphic units are described, and the geologic formations composing each unit discussed. Attention will be given to the lithology, mineralogy, and water-bearing characteristics of the geologic units where information is avaliable. The location of the geomorphic units are illustrated on plate 1*A*.

(1) *Sierra Nevada*. The Sacramento Valley is bounded on the east by the mountainous Sierra Nevada, a massive block of the Earth's crust that has been uplifted and tilted westward. The block extends under the sediments of the valley and underlies the eastern part at depth. The Sierra Nevada is composed of intrusive igneous rocks, metamorphosed volcanic rocks, and Paleozoic sedimentary rocks. The intrusive rocks are mainly granodiorite and quartz diorite with andesitic and rhyolitic extrusive rocks. In addition to the feldspars, quartz, and biotite of the igneous rocks, a wide variety of other minerals is present. These include cal-

cite, magnesite, barite, serpentine, metal sulfides, and others. The massive rocks of the Sierra Nevada contain little water, with the little that is available occurring in joints and fractures. The water quality of streams draining the Sierra Nevada is generally very good.

(2) *Coast Ranges.* The Coast Ranges, adjacent to the west of the valley, consist of Cretaceous marine sedimentary rocks folded and uplifted into ridges trending northwest-southeast, parallel to the valley. The Cretaceous rocks dip eastward and underlie much of the Sacramento Valley at depth. Also present in the Coast Ranges is the Franciscan Complex, which consists of highly metamorphosed marine sedimentary rocks of late Mesozoic age. The major rock type is this geologic unit is greywacke, interbedded with shales and minor limestone units. The primary minerals of the sedimentary rocks are plagioclase and quartz. Many lithic fragments present contain chert, chlorite, and mica. Ultramafic minerals have been metamorphosed to serpentine and magnesite. The marine sedimentary rocks are mostly consolidated and contain little water. Some units retain connate saline water, and streams draining the Coast Ranges may be contaminated by saline springs.

(3) *Cascade Range.* Between Oroville and Red Bluff, the northeastern part of the Sacramento Valley is bounded by the Cascade Range geomorphic unit. Adjacent to the valley, this unit is composed of the gently southwestward dipping Tuscan Formation of Pliocene age. On the surface, the Tuscan Formation is extensively eroded, and southwestward flowing streams have incised deep canyons. Beneath the valley, the Tuscan extends westward under younger valley sediments as far as the Sacramento River, and there the Tuscan interfingers with the Tehama Formation. The Tuscan is composed of volcanic breccia, coarse- to fine-grained tuffs, and volcanic sands, all of primarily andesitic composition. The most abundant mineral in the black sands found in wells drilled into this unit is plagioclase, and accessory quartz and pyroxenes. Volcanic glass is also abundant from the mudflow and tuff deposits. The Tuscan is an important aquifer in the northeastern part of the valley, and it contains fresh water at all depths.

(4a) *Low hills and dissected uplands, east side.* The dissected alluvial uplands leading up to the Sierra Nevada on the east side of the valley are composed of Tertiary and lower Quaternary sediments. This gently rolling terrain merges with the foothills of the Sierra Nevada to the east and the low alluvial plains to the west. The oldest rocks here are of the Eocene Ione Formation, overlain by the Oligocene, Miocene, and Pliocene volcanic deposits of the Valley Springs and Mehrten Formations. These units extend westward to the trough of the valley, but they are generally too deep to be tapped as aquifers except in the foothills area. Overlying the volcanic sediments are upper Tertiary and Quarternary continental deposits eroded from the Sierra Nevada. The older Tertiary volcanic sediments are composites of volcanic sands, ash and mudflows, and tuff layers of rhyolitic and andesitic composition. Particular minerals noted in these units include biotite, hornblende, orthoclase, plagioclase, and quartz. The Ione Formation contains kaolinitic clay layers. The younger deposits, the Laguna Formation and Fair Oaks Formation of Shlemon (1967), are sand, gravel, and silt deposits intercalated by clay layers. The Quaternary deposits are poorly sorted, and wells finished in these units produce only moderate quantities of water.

(4b) *Low hills and dissected uplands, northeast.* The low hills on the northeast margin of the valley consist of reworked sediments eroded from the underlying Tuscan Formation. The hills show the characteristic form of alluvial fans but are deeply trenched by the streams draining the Cascade Range. These fanglomerate deposits, as they are called, are mainly cemented sands, gravels, and silts, and have a mineral composition similar to that of the Tuscan Formation from which they are derived. The fanglomerate is also an important source of water in this area.

(4c) *Low hills and dissected uplands, west side.* The low hills on the west side of the valley are composed of the Tehama Formation of Pliocene age. These deposits extend from Red Bluff on the north almost as far south as Fairfield. The Tehama is made up of poorly sorted fluviatile sediments, primarily beds of sandy silt and silty clay with some lenses of crossbedded sands and gravels. Many of the coarser layers are cemented by calcium carbonate that reduces their permeability. The Tehama extends eastward to about the middle of the valley and is generally within 150 to 200 feet of land surface. Tectonic activity since deposition has folded the Tehama into a number of structures such as the Dunnigan Hills, Corning Ridge, and Plainfield Ridge along the valley margin. Sediments originated in the Coast Ranges and are rich in plagioclase and magnesium silicates, such as chlorite and serpentine. The Tehama is an important potential aquifer, although currently most water is the area is being pumped from more permeable alluvial fan deposits nearer the surface.

(5a) *Alluvial plains and fans, east side.* The alluvial plain on the east side of the valley is referred to as the Victor Plain by Olmsted and Davis (1961). The Victor Formation[2] of Olmsted and Davis (1961), which

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[2] Recent work of Marchand and Allwardt (1981, p. 207) virtually eliminates the use of the Victor Formation for the northeastern part of the San Joaquin Valley. However, because no similar recent work has been done in the Sacramento Valley, the Victor Formation as defined and mapped by Olmsted and Davis (1961, p. 93) is used in this report.

ranges in thickness from 50 to 100 feet, covers the surface throughout the area and overlies the Laguna Formation, a Pleistocene continental deposit. The plain extends from the northern San Joaquin Valley to north of Chico, where it pinches out between the fanglomerate of the Cascade Range and the Sacramento River flood plain. The Victor Formation is composed of alluvial sediments carried down from the Sierra Nevada and contains numerous channel deposits. The sediments become generally finer grained towards the west with bluish- and greenish-gray clays indicating reducing deposition environments near the center of the valley. Opposite the Sierra Nevada, the material contains extensively weathered feldspars, quartz, mica, biotite, and layers of arkosic sandstones. Opposite the Cascade Range, the Victor Formation is composed of reworked volcanic detritus from the Tuscan Formation. Water is generally available throughout the Victor Formation, though many high-capacity irrigation wells also tap the underlying Laguna Formation.

(5b) *Alluvial plains and fans, west side.* The low alluvial fans on the west side of the valley have been laid down by streams draining the Coast Ranges. The fans are aggrading and have poorly developed soil horizons. The northernmost fan is that of Stony Creek, which extends from the valley margin to the Sacramento River. South of this fan, a series of small fans built up by ephemeral streams extends only a short distance away from the Coast Ranges. Cache Creek and Putah Creek, south of the Dunnigan Hills, also have developed rather large fans which coalesce to form Putah Plain. The lithology of these fans is varied but generally is coarse-grained and poorly sorted. The mineralogy reflects the source areas in the Coast Ranges. The alluvial fans are generally good aquifers, especially where old stream channel deposits are penetrated.

(6) *Flood basins.* Low areas adjacent to the Sacramento River were subject to frequent flooding before extensive construction of levees in modern times. In these basins, fine-grained sediments have settled out of flood waters to form poorly permeable deposits. Deposits between 50 and 170 feet thick of yellow clay, indicating oxidizing conditions, overlie blue clays reflecting reducing conditions at depth. Few wells are drilled in these areas, and the only water generally available is in tongues of sand and gravel from old channel deposits.

In Sutter Basin, ground water contains high chloride concentrations and is unsuitable for irrigation purposes. The origin of this high chloride water is thought to be from Cretaceous marine sedimentary rocks brought closer to the surface by faulting associated with the formation of Sutter Buttes.

(7) *Stream channels and natural levees.* Along the major rivers and streams throughout the valley, Holocene alluvial deposits form flood plains and natural levees. The levees slope gently away from the channels and merge into the surrounding flood basin deposits. The deposits are generally coarse grained and poorly sorted. The varied mineralogy reflects the many sources from which these sediments are derived. Wells drilled in these deposits are hydraulically connected to the adjacent rivers and can produce large quantities of water.

(8) *Sutter Buttes.* Sutter Buttes, a volcanic neck of late Tertiary age, rises abruptly 2,100 feet above the surrounding plains. The core of the buttes is andesite, surrounded by alluvial fans created from the erosion of the igneous rocks. The deposits are poorly sorted and contain tuff, volcanic breccia, and sands. Some Cretaceous marine sedimentary rocks exposed at the buttes were forced upwards by the rising lava. The volcanic rocks yield little water, but the adjoining alluvium produces moderate amounts.

HYDROGEOLOGY

The direction of ground-water movement can be determined from the configuration of the water table where ground water occurs in saturated sediments and is not confined. Ground-water movement is influenced by gravity, and so is downhill as determined by the altitude of the water table. Plate 1*B* is a map showing lines of equal altitude of the water table for the Sacramento Valley in the spring of 1975. Although extensive changes occurred in some areas during the drought of 1976 and 1977, the 1975 map reflects the general conditions throughout the valley as they existed when most of the water-quality samples were collected during the mid-1970's.

In the north part of the valley, ground waters flow to the south and away from the valley walls. The Sacramento River is a gaining stream north of Colusa and is a major ground-water discharge zone in the north part of the valley. Stony Creek alluvial fan is a particularly important area for recharge. South of Colusa, the Sacramento River becomes a losing stream, contributing water to the adjacent sediments. In the west-central part of the valley, between Colusa and Woodland, recharge from the west infiltrates the valley sediments and moves toward pumping depressions east of the Dunnigan Hills. In the east-central part of the valley, from Oroville to Marysville, the Feather, Yuba, and Bear Rivers recharge the ground water near the valley margin. Once on the valley floor, the Feather River becomes a gaining stream east of Sutter Buttes, but below Marysville it begins to lose water to pumping depressions to the east and west. A large pumping depression in the southeast draws water from the American and Sacramento Rivers in the vicinity of Sacramento. In the southwest, much ground-water recharge occurs in the Cache and Putah Creek alluvial fans. This water moves eastward toward pumping depressions near Woodland and Davis. Some recharge from Cache Creek flows around the end of the Dunnigan Hills to pumping depressions north of Woodland.

The water table in the Sacramento Valley is generally close to the surface, and in only a few places is it more than 80 feet below the surface. Depth to water in the flood basins and alluvium along the Sacramento and Feather Rivers ranges from 10 to 20 feet. This very shallow water table extends eastward to include much of the western part of the Victor Plain. In the alluvial fans along the west side of the valley, the depth to water is between 10 and 40 feet. Lowering of water levels in pumping depressions north of Woodland and south of Davis, however, has increased the depth to water in those places. Along the southeast margin of the valley, the depth to water increases from less than 10 feet, near the flood basins, to more than 80 feet in the foothills. In the fanglomerate of the Cascade Range around Chico, the depth to water is generally 10 to 40 feet.

The valley boundary illustrated on plate 1*B* is the approximate boundary of the principal alluvial aquifers currently used in the Sacramento Valley. There is no single definition of the Sacramento Valley, and different boundaries are drawn for different purposes. The boundary shown is approximately that used in a ground-water-flow model of the Sacramento Valley (California Department of Water Resources, 1978a, Appendix A). However, the definition of the Sacramento Valley ground-water basin by the State of California encompasses a much larger area. The boundary is a reference shape to show continuity among illustrations.

On the east side of the valley, the margin coincides with the contact between the alluvium of the low hills and dissected uplands geomorphic province, and the older rocks of the Sierra Nevada and Cascade Range provinces. On the west side, the division is at the contact between the younger alluvium of the alluvial fans and plains, and the older alluvium of the low hills and dissected uplands geomorphic province. This allows delineation of the Dunnigan Hills, and excludes a large, undeveloped and sparsely populated area to the northwest of the valley.

Some wells outside the principal alluvial aquifers were included in the data analysis, as the boundary of those aquifers is somewhat arbitrary. Because these wells lie in recharge zones, their characteristics are important to an understanding of ground-water chemistry in the rest of the valley, even though they are outside the area of the principal alluvial aquifers.

HYDROCHEMICAL FACIES

The concept of hydrochemical facies as described by Back (1966) is used to designate zones or areas in which ground waters share unique chemical characteristics. The differences between facies reflect different controls on water chemistry from the lithology and mineralogy of, flow patterns in, and sources of recharge to an aquifer. The prefix "hydro" is used as a modifier of "chemical" to emphasize the interdependence of chemistry and hydrology. The ground water in the Sacramento Valley shows a great diversity in chemical compositions. By dividing the valley into hydrochemical facies, the differences can be better related to differences in the sedimentary matrix holding the water and the sources of ground-water recharge.

CRITERIA AND PROCEDURE FOR DIVISION

While hydrochemical facies have commonly been defined in terms of water types (as determined by the predominance of ions in terms of equivalents per million; Back, 1966), the definition of hydrochemical facies can be based on any unique chemical signature. For the Sacramento Valley, this division was accomplished using differences in the concentrations of some of the dissolved chemical constituents.

An initial division of the valley was attempted by studying maps showing the geomorphic units, the water table, and the distribution of individual chemical constituents. Outlines of these areas were drawn up to the nearest quarter township, and a tentative hydrochemical facies was determined for each well. This initial division broke the valley into three areas extending northwest-southeast, parallel to the axes of the valley—along the west side, the east side, and in the central basins. Each of these areas was divided into a northern and southern part resulting in six tentative divisions.

After this initial division, these six areas were tested to determine if they could be successfully differentiated on the basis of their chemistries. Linear discriminant function analysis (Davis, 1973; Drake and Harmon, 1973) was used for this purpose. In linear discriminant function analysis, a linear combination of variables is used to distinguish between previously defined groups. After the function is defined, it can be used to classify new samples of unknown origin into one of the original groups.

To determine which chemical constituents would be the best to use in the discriminant analysis, the amount of variation in the major chemical species associated with the differences between hydrochemical facies was determined. The results of this analysis of variance are shown in table 1. The first five species in this table

TABLE 1.—*Variation in chemical constituents explained by variations between hydrochemical facies*

Constituent	Percent variation explained
Silica	62.7
Boron	48.5
Sodium	44.7
Bicarbonate	39.4
Nitrate	36.8
Chloride	30.1
Magnesium	27.2
Calcium	15.1
Sulfate	9.6

were picked for the analysis. Because chloride is closely associated with sodium in the valley, it was passed over and magnesium added to give a total of six chemical constituents to use in the discriminant analysis.

Of the 671 chemical analyses available, only 340 had measurements for all the species and could therefore be used in the analysis. Most of the reduction in sample size was due to the much smaller number (358) of silica analyses. However, because silica showed by far the greatest amount of variation between the tentative hydrochemical facies, it was decided to use silica at the cost of reducing the number of samples that could be classified using the discriminant function. Samples, which lack measurements of all six of the chemical species used, were subsequently classified on the basis of nearby wells.

About one-fifth of the eligible samples were used to define the discriminant functions for the six hydrochemical facies. Using these functions, the remaining eligible samples were classified using the chemistry, and this classification was compared to the prior classification from the map data. Misclassified observations were of two types. Type 1 misclassifications were scattered throughout other facies and showed no pattern nor were particularly close to the boundary between two areas.Type 2 misclassifications were clustered in an adjacent hydrochemical facies near the boundary. In the latter case, the boundaries were redrawn and the chemical analyses reclassified.

The discriminant functions were recalculated several times with adjustments in boundaries between each calculation. The final analysis showed that 76 percent of the samples could be correctly classified by hydrochemical unit using the six chemical species. Thirteen percent of the samples were misclassified into the adjacent northern or southern portion in the same part of the valley, indicating an association between west side, east side, and basin pairs. On the basis of the classification of wells in a quarter township, each quarter township was assigned to its final hydrochemical facies. Other wells missing some of the chemical species used for the classification were classified by their quarter township location.

The discriminant analysis showed that enough chemical variation existed among the six hydrochemical facies to consider them chemically distinct. The final boundaries of the hydrochemical facies are shown on plate 1*B*. On the east side of the valley, one of the facies lies opposite the Cascade Range, and one opposite the Sierra Nevada. The flood basins along the axis of the valley are divided into two more facies, one in Butte Basin and including Sutter Buttes, the second in the Colusa, Sutter, and American Basins. The final two hydrochemical facies are opposite the Coast Ranges and are divided north and south near Colusa. In the next section, the chemical characteristics of the six hydrochemical facies are presented and compared, and differences in chemistry are discussed.

DESCRIPTIONS OF HYDROCHEMICAL FACIES

Table 2 shows the geometric mean, minimum, and maximum of chemical concentrations for each of the hydrochemical facies. To determine if the average concentrations of chemical species in the hydrochemical facies are significantly different, the differences between geometric means were tested using a *t* test. The results of these comparisons are illustrated quantitatively in the same table.

TUSCAN VOLCANIC ROCKS

The Tuscan volcanic rocks hydrochemical facies is along the northeastern margin of the Sacramento Valley (pl. 1*B*) adjacent to the Cascade Range. The geologic formations in this area are the Tuscan Formation and more recent alluvial sediments derived from erosion of the Tuscan. Recharge is from the Cascade Range geomorphic province, and ground water is either discharged to the Sacramento River or moves into Butte Basin south of Chico. The Tuscan and its derivatives contain andesitic sands and extensive tuff deposits. Volcanic glass and plagioclase are abundant in these sediments.

The chemistry of ground water in the area reflects the low concentrations of dissolved solids carried by recharge from the Cascade Range, having low mean concentrations of magnesium, sodium, bicarbonate, sulfate, and chloride. Silica concentrations are high due to solution of volcanic glass, and the facies has the highest average nitrate-nitrogen concentration of the six. The maximum boron concentration is rather high, although the mean concentration is only moderate. Boron in excess of 1.0 mg/L occurs in only three wells, all to the east of the Sacramento River northeast of Red Bluff.

TABLE 2.—*Geometric mean, minimum, and maximum of chemical concentrations for each of the hydrochemical facies, Sacramento Valley*

[Figure above line refers to geometric mean; figures below line refer to minimum-maximum range. H, high; L, low; VH, very high; VL, very low. NOTE.—These comparisons are relative to the other hydrochemical facies and do not necessarily describe the absolute values. Labels were assigned only where the difference between two geometric means tested significant at the 95 percent level]

Chemical species	Tuscan volcanic rocks	Victor Plain	Butte Basin	Sutter Basin	North alluvial fans	South alluvial fans
Dissolved solids (mg/L)	L 231 137–571	L 220 137–1100	290 129–723	H 400 97–2040	280 108–1170	H 400 175–1420
Calcium (mg/L)	26 14–75	L 21 5.7–170	32 5.5–98	32 6.9–220	H 39 8.2–99	H 39 13–140
Magnesium (mg/L)	L 19 9.1–60	VL 12 3.6–120	24 5.0–93	24 2.2–160	24 7.6–70	H 33 3.5–140
Sodium (mg/L)	L 14 3.9–68	19 7.2–180	20 6.3–93	H 55 5.9–360	22 7.5–240	H 52 15–320
Potasium (mg/L)	1.3 0.3–5.9	1.3 0.4–4.5	H 1.9 0.6–5.0	H 1.7 0.3–5.4	L 0.8 0.4–2.1	1.2 0.2–7.0
Bicarbonate (mg/L)	L 170 98–400	VL 130 68–504	230 44–522	H 270 70–897	240 83–560	VH 310 130–1060
Sulfate (mg/L)	L 8.1 0.0–71	L 8.0 0.2–140	12 0.5–150	17 0.3–590	18 1.6–400	21 1.8–180
Chloride (mg/L)	VL 6.5 0.9–97	15 2.0–380	L 11 1.0–210	H 31 2.4–920	15 2.7–170	H 37 2.2–580
Fluoride (mg/L)	0.11 0.1–0.3	0.18 0.1–10.0	0.12 0.1–0.3	0.11 0.0–0.4	0.16 0.0–0.6	H 0.29 0.1–1.0
Nitrate - N (mg/L)	H 2.7 0.2–27	0.81 0–61	1.0 0–20	L 0.12 0–14	1.7 0.01–11	1.8 0–12
Phosphate - P (mg/L)	0.05 0.0–0.31	0.11 0.01–0.39	0.11 0.01–0.45	0.15 0.01–0.50	0.06 0.02–0.30	0.07 0.01-0.42
Silica (mg/L)	H 51 35–67	H 55 25–74	H 51 31–75	39 23–73	L 26 8.5–52	L 28 12–54
Iron (µg/L)	4.8 0–170	5.2 0–600	8.0 0–1900	H 11 0–520	9.7 0–280	8.0 0–180
Manganese (µg/L)	3.4 0–10	5.5 0–280	9.1 0–1700	H 75 0–2300	8.0 0–70	2.8 0–2000
Arsenic (µg/L)	1.2 0–4	2.2 0–20	H 5.5 0–50	H 5.8 0–100	1.7 0–6	2.3 0–31
Boron (mg/L)	0.066 0–1.50	L 0.023 0–0.60	L 0.034 0–0.37	H 0.140 0–1.10	0.068 0–0.58	VH 0.400 0–8.10

The source of the high boron water is Tuscan Spring, located along Salt Creek in Tehama County in section 32 of township 28 N., range 2 W. (Waring, 1965).

VICTOR PLAIN

The Victor Plain hydrochemical facies is along the east and southeast margin of the valley, and extends westward to near the Feather and Sacramento Rivers. Recharge is primarily from the Sierra Nevada to the east, although pumping depressions southeast of Marysville and north of Sacramento induce recharge from the rivers. North of Marysville, water is discharged into the Feather River or passed into Butte Basin. South of Marysville, most of the ground-water discharge seems to be by pumping. Along the valley margin, the aquifers are volcanic sands with associated tuffaceous deposits. In the central and western parts of this facies, the volcanic units dip under the Victor Formation composed of alluvium from the Sierra Nevada.

The Victor Plain facies has a low average dissolved-solids content reflecting recharge from the Sierra Nevada. Concentrations of calcium, magnesium, bicarbonate, boron, and sulfate are all low in this area. Silica is high, reflecting the volcanic material present in the sediments.

BUTTE BASIN

The Butte Basin hydrochemical facies roughly coincides with the Butte flood basin east of the Sacramento River. The basin extends from Chico on the north to Yuba City on the south and lies between the Feather and Sacramento Rivers. Sutter Buttes is included in this facies as too few chemical analyses were available from this area to justify a separate facies. The basin receives recharge from the Tuscan volcanic rocks facies and from Victor Plain to the east. A small amount of recharge also occurs in the vicinity of Sutter Buttes. Ground water leaves the Butte Basin facies to enter the Sacramento River and to enter the Sutter Basin facies east of Sutter Buttes. In the flood basins the sediments are fine grained and reducing.

Ground water in the Butte Basin facies has a somewhat higher average dissolved-solids concentration than the two eastern margin facies possibly reflecting longer subsurface residence times or a change in sediment lithology. Chloride and boron are the only two species that have low average concentrations in this facies. The high silica concentrations may be a result of recharge from the Tuscan volcanic rocks facies and from volcanic material around Sutter Buttes. High arsenic concentrations imply deposition in a reducing environment (Garrels and Christ, 1965). This facies has the highest average potassium concentration, which may reflect the longer residence times or a change in mineralogy of the sediments.

Information on the variation in water chemistry with depth was obtained from a U.S. Geological Survey test well drilled in section 32 of township 19 N., range 1 W. Three piezometer tubes were installed at different depths and isolated by cement packers. Data on the shallow water at the site are available from a previous study (Fogelman, 1976).

Analyses from the three piezometers and from the shallow water are shown in table 3. The percent composition of the major ionic species in terms of milliequivalents per liter are provided in figure 3. Between 80 and 595 feet, a decrease in magnesium is balanced by an increase in sodium, with calcium remaining about the same. There is a slight increase in the percent of chloride in the ground water over this same interval, but the net change in anion composition is very small. Below 595 feet, however, calcium and magnesium decrease, both in percent composition and concentration, and sodium increases. Chloride also increases, becoming the dominant anion by a depth of 968 feet. Even at 1,333 feet, however, the dissolved-solids concentration of the water is only moderate, at 526 mg/L, and the boron concentration remains low.

SUTTER BASIN

The Sutter Basin hydrochemical facies is between the Sacramento and Feather Rivers south of Sutter Buttes. This facies extends west of the Sacramento River near Colusa to include part of Colusa Basin and includes some of the American Basin east of the Feather River. Recharge comes from Sutter Buttes, from the Butte Basin hydrochemical facies east of Sutter Buttes, and from both the Sacramento and Feather Rivers. Sediments in the flood basins are generally fine grained and reducing at depth.

The Sutter Basin facies is tied with the south alluvial fans facies for the highest average dissolved-solids concentration. This facies is also high in sodium, chloride, bicarbonate, potassium, and boron. The effects of reducing conditions are evident in the relatively higher concentrations of iron, manganese, and arsenic in this area, all of which are more soluble in reducing environments (Garrels and Christ, 1965). The very low average nitrate concentration in this facies is also indicative of reducing conditions, where nitrate can be removed by denitrification reactions.

The origin of the high dissolved-solids water is thought to be connate marine water moving upward along fault zones created when Sutter Buttes was emplaced (Curtin, 1971). Throughout much of the southern part of Sutter Basin, water of very high salinity (specific conductance greater than 3,000 micromhos) is located within 400 feet of the surface.

TABLE 3.—*Chemical composition of water from wells of various depths, section 32 of township 19 N., range 1 W.*

Sample No. (fig. 3)	Site identification	Depth of well (feet)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Bicarbonate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Nitrate-N (mg/L)	Boron (mg/L)	Dissolved solids (mg/L)
1	19N/01W–32A01M	80	28	24	34	260	12	12	0.59	0.12	276
2	19N/01W–32G03M	595	25	4.4	62	210	12	22	.03	.15	276
3	19N/01W–32G02M	968	12	2.6	110	150	3.6	110	.02	.18	340
4	19N/01W–32G01M	1,333	15	2.8	160	110	3.4	230	.12	.24	526

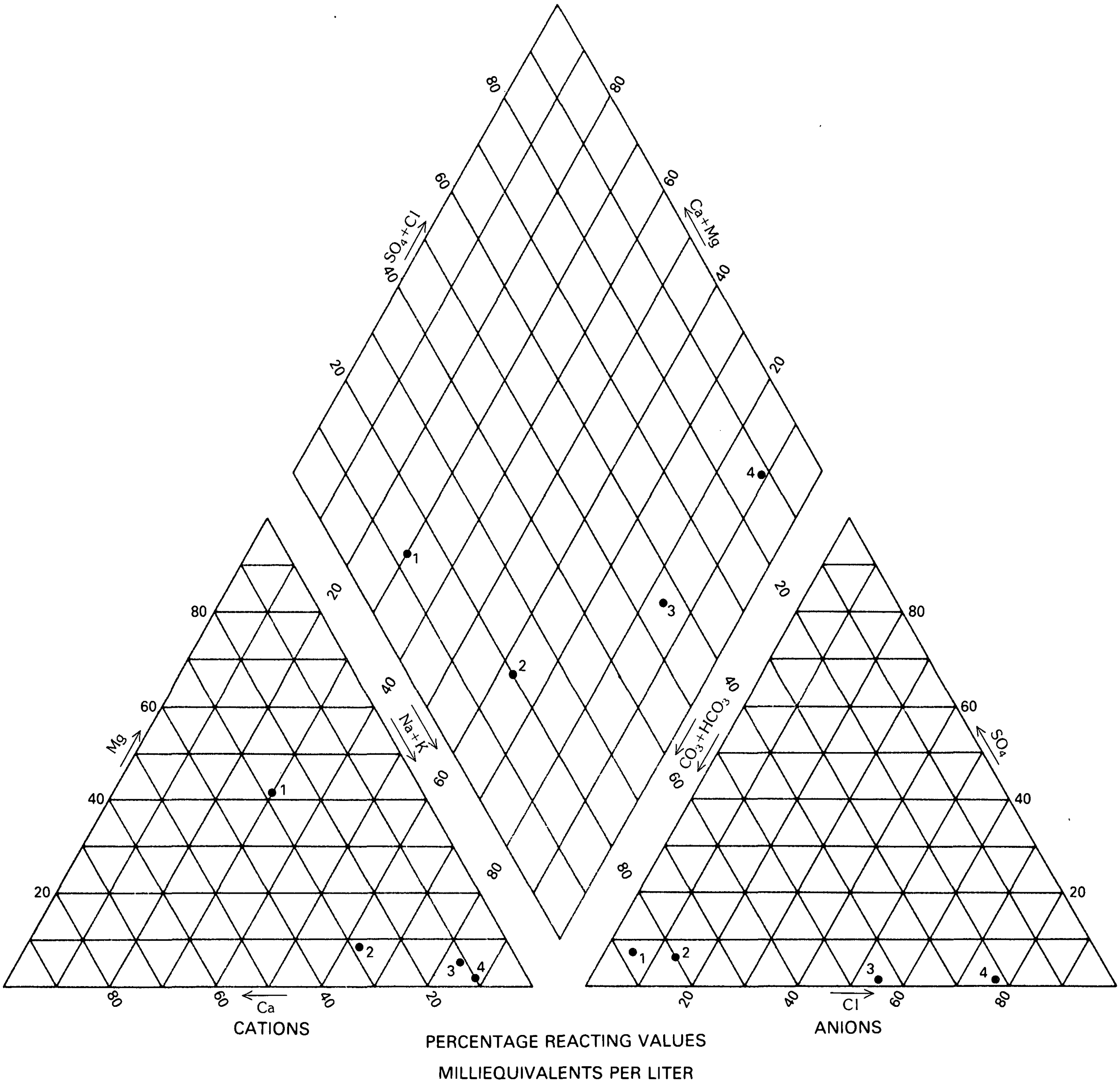

FIGURE 3.—Major-ion composition of water from wells of various depths in section 32 of township 19 N., range 1 W. Numbers refer to sample numbers in table 3.

NORTH ALLUVIAL FANS

The north alluvial fans hydrochemical facies is along the northwestern margin of the valley. Ground water occurs primarily in alluvial fan deposits and is recharged by streams draining the Coast Ranges. The alluvial fan of Stony Creek is a major source of recharge in this area, with flow radiating away from the fan to the north, east, and south. Ground-water flow in this facies is generally east and south. Most of the water is discharged to the Sacramento River along the eastern margin of the facies, although some moves into Colusa Basin along the southern boundary. Sediments in the alluvial fans are primarily derived from Mesozoic marine rocks of the Coast Ranges with sediments derived from Franciscan metamorphic rocks carried down by some of the larger streams.

The average dissolved-solids concentration in the north alluvial fans facies is moderate, and most of the chemical-constituent averages fall between those of the other facies. Calcium is the only species with a high average concentration in this facies; this is from the waters of Stony Creek, which are high in calcium. Silica is much lower in waters on the west side of the valley, and this is shown by the low average silica concentration.

SOUTH ALLUVIAL FANS

Located along the southwestern margin of the valley in alluvial fans adjacent to the Coast Ranges, the south alluvial fans hydrochemical facies extends from Putah Creek north to township 15 N. Recharge from the Coast Ranges is provided by numerous ephemeral streams north of township 10 N., and by Cache and Putah Creeks in townships south of 11 N. Recharge from Cache Creek moves around the end of the Dunnigan Hills to pumping depressions north of Woodland. Some recharge is also drawn from the Sacramento River to these same pumping depressions.

The south alluvial fans hydrochemical facies is distinguished by having high average concentrations for many of the chemical species measured. Dissolved solids, calcium, magnesium, sodium, chloride, and fluoride all have high average concentrations here. Boron and bicarbonate concentrations in this facies average very high. With little volcanic material to provide silica, its average concentration is low, as in the north alluvial fans.

Boron and chloride concentrations in the ground water of this facies average the highest in the valley, and boron concentrations as high as 8.1 mg/L have been measured in township 11 N., range 2 E. The source of the chloride and boron has been attributed to the streams draining the Coast Ranges (Bertoldi, 1976). Information obtained from a deep test well drilled by the U.S. Geological Survey in section 34 of township 12 N., range 1 E., indicated another possible source. The test well 12N/01E–34Q was drilled to a total depth of 2,400 feet and piezometers tubes installed at 942 feet, 1,396 feet, and 2,120 feet. No sample was obtained from the 942-foot depth, but analyses from the two deeper piezometers are shown in table 4. At a depth of 2,120 feet, water containing 12 mg/L boron and 660 mg/L chloride was encountered. Piezometric heads in the test well indicate upward movement of water, which may be contaminating the shallow water.

The source of boron and chloride in the streams draining the Coast Ranges is warm saline springs, a number of which occur in the Clear Lake area. Partial chemical analyses from these springs are also shown in table 4. Boron concentrations are as high as 310 mg/L in these springs. To determine the source of the high boron concentrations in the ground water in township 11 N., range 2 E., the percent composition in milliequivalents per liter of the wells in this township were plotted along with the deep well water and the warm spring water (fig. 4). The Wilbur Oil Test is a wildcat oil well that produces cold water also high in boron and chloride.

TABLE 4.—*Data for wells and springs plotted in figures 4 and 5*

[Samples 1–2 from U.S. Geological Survey test well; 3–9, reported by Fogelman (1976); 10, average for 1960–76; 11–15, reported by White and others (1973), with locations as indicated therein]

Sample No. (fig. 4)	Site identification	Depth to first opening (feet)	Dissolved solids (mg/L)	Chloride (mg/L)	Boron (mg/L)	Temperature (°C)
1	12N/01E–34Q01M	2,120	1,310	660	12	21.0
2	12N/01E–34Q02M	1,396	482	95	1.1	21.5
3	11N/02E–20K06M	387	1,060	210	3.7	20.0
4	11N/02E–18R01M	264	321	39	1.4	18.5
5	11N/02E–18C02M	205	1,470	210	8.1	18.0
6	11N/02E–23N02M	200	746	66	2.5	21.0
7	11N/02E–14B03M	198	307	37	1.1	17.5
8	11N/02E–30C01M	184	741	96	3.3	18.0
9	11N/02E–29A02M	151	816	140	4.8	18.0
10	Cache Creek at Capay	---	268	36	1.5	---
11	Wilbur Springs	---	27,134	9,700	310	55.0
12	Elgin Mine Spring	---	28,872	11,000	240	68.5
13	Abbott Mine Spring	---	7,250	1,900	56	≈30
14	Grizzly Spring	---	12,400	3,940	178	17.5
15	Wilbur Oil Test	---	19,080	11,400	23	21.3

From figure 4 there is no clear indication of whether the water in the wells (sample Nos. 3–9) is derived from the thermal springs (sample Nos. 11–14) or from deep ground water in the area (sample No. 1). Two of the thermal springs, Wilbur Oil Test well and the deep well, are very high in percent sodium. Two of the thermal springs show an increase in percent magnesium, but the percent calcium remains very low.

The deep ground water and the Wilbur Oil Test well have a much higher percentage of chloride than the thermal springs, which are enriched in carbon dioxide from metamorphism at depth (Barnes and others, 1973). As no clear trends emerged in the plot of the percent compositions in milliequivalents per liter, a second plot of chloride versus boron concentrations was made (fig. 5). The dashed diagonal line in figure 5 represents the dilution of Wilbur Springs water with water containing no boron or chloride. The thermal springs all plot very close to this line, having both high chloride and boron concentrations. The shallow wells in township 11 N., range 2 E., all plot very close to the the line representing dilution of Wilbur Springs water, as does the average composition of Cache Creek. Wilbur Oil Test well and the deep wells in the valley plot to the right of the dilution line, which indicates more chloride relative to boron in these waters. From figure 5 the source of the high chloride and boron concentrations is confirmed as water from the thermal springs in the Coast Ranges carried into the valley by streams, such as Cache Creek. Distinct differences between the cold waters,

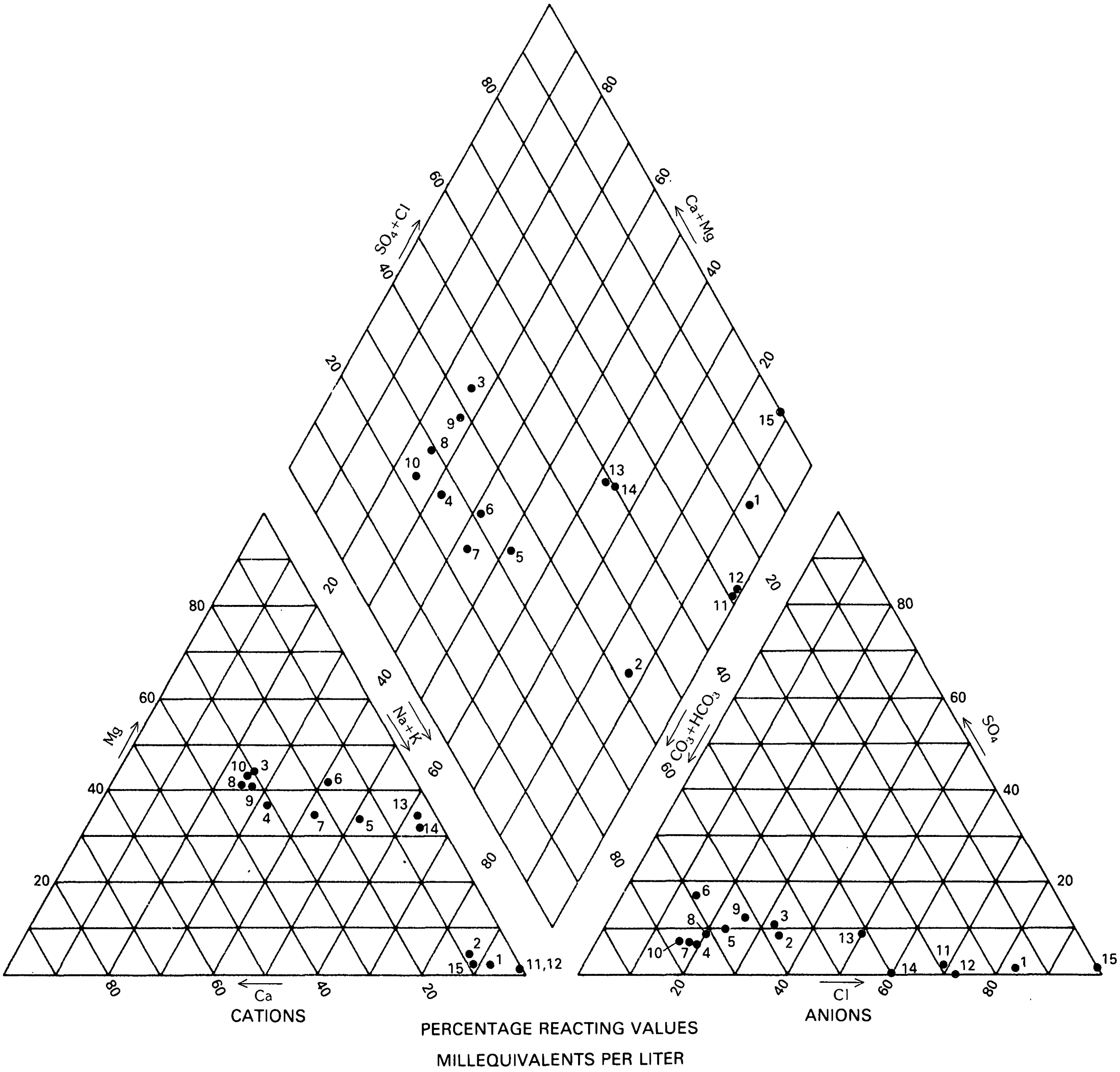

FIGURE 4.—Major-ion composition of water from springs in the Clear Lake area and from wells in a high boron area northwest of Woodland. Numbers refer to sample numbers in table 4.

such as Wilbur Oil Test and well 12N/01E–34Q01, and the thermal waters can be found in the boron-to-chloride ratio and the percent of bicarbonate ion in the waters. The hot waters probably receive inputs of carbon dioxide and boron from a gas phase produced during metamorphism of the marine sediments at depth. Cold waters are not enriched in volatile components and therefore have lower boron-to-chloride ratios and lower percent bicarbonate contents. The shallow wells in township 11 N., range 2 E., have the higher boron-to-chloride ratios indicative of a thermal water source.

TEMPORAL CHANGES

Ground-water-quality degradation may be occurring in the Sacramento Valley because of increasing development accompanied by more intensive agriculture and denser habitation. Such effects have been noted in the

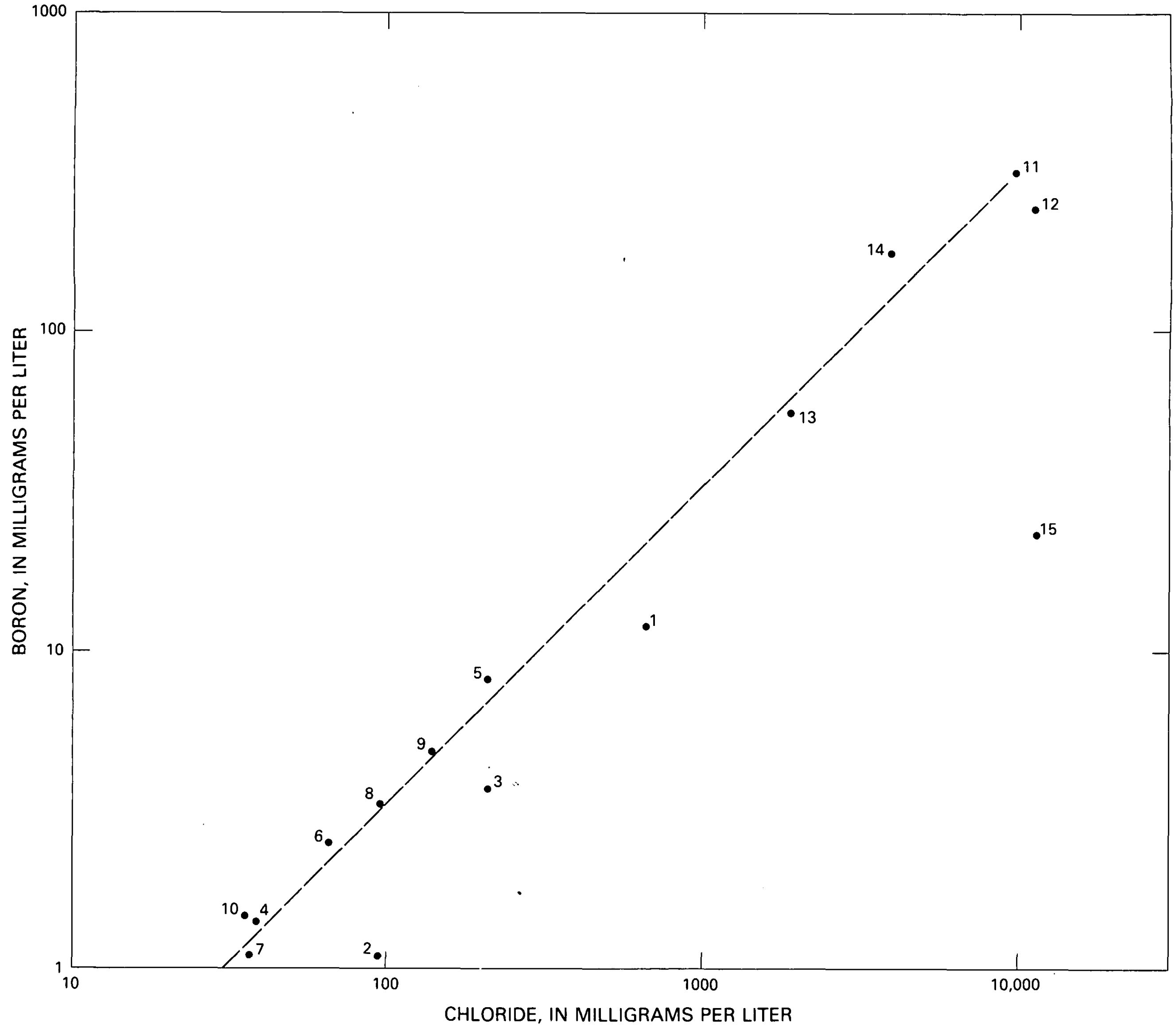

FIGURE 5.—Plot of chloride versus boron for springs in the Clear Lake area and for wells in a high boron area northwest of Woodland. Numbers refer to sample numbers in table 4. Dashed line indicates dilution of Wilbur Springs water with water containing no boron or chloride.

San Joaquin Valley (Kern County Water Agency, 1979), in San Bernardino County (Klein and Bradford, 1979), and in the Colorado River Basin (El-Ashry, 1980). Much of the problem is related to infiltrating irrigation water that (1) has been concentrated by evapotranspiration, (2) has dissolved salts added as fertilizers and soil conditioners, and (3) has leached natural salts from the unsaturated zone. Additional degradation can occur from nonagricultural activities, such as the disposal of sewage and industrial wastes.

In this section, water-quality data from the Sacramento Valley are examined for linear trends with time. Data in each of the hydrochemical facies are combined to derive an average trend for each of the areas. Individual wells are also examined for temporal changes to show more localized variations. The locations of wells used to study the temporal changes are plotted on a map of the valley, and those wells showing significant changes are labeled with symbols indicating the direction of change (pl. 2).

Two variables are used in this study, dissolved-solids and nitrate concentrations. Dissolved solids measures the total amount of dissolved chemicals in a water, and it gives a general indication of overall water quality. Nitrate is derived from a number of potential pollution sources, such as fertilizers and sewage. Increases in nitrate would indicate specific influences of man's activities. These two variables will give a fairly comprehensive evaluation of any temporal changes that may be occurring.

METHODS OF DATA ANALYSIS

To determine the average changes occurring in a hydrochemical facies, some technique was needed so that wells with different average dissolved-solids or nitrate concentrations could be compared. This was accomplished by standardizing the data for each well to have a mean of zero and a standard deviation of one. Data from all the wells for each year could then be averaged with equal weight being given to each well. This data manipulation procedure produced a data set with one observation per year for the period of record in each hydrochemical facies. The yearly observations represented the average for all the wells for which data were available in each hydrochemical facies.

Trends in the chemistry of the facies were then studied using a linear regression of the standardized and averaged dissolved-solids or nitrate concentrations versus time. One of the fundamental assumptions of regression analysis is that the observations are independently distributed. For sequences of data collected over time, this requirement is sometimes violated because the data are autocorrelated. Because of memory effects in natural processes, measurements taken at one time may be correlated to measurements taken at previous times.

To test the extent to which the dissolved solids and nitrate data suffered from autocorrelation problems, lag one serial correlations were calculated, and cumulative frequency histograms of these autocorrelations compiled. Matalas, Slack, and Wallis (1975) have generated a series of empirical cumulative frequency histograms for data sequences having a range of serial correlations. By comparing the cumulative frequency histograms for dissolved solids and nitrate in the Sacramento Valley to these empirical histograms, the probable population autocorrelations were determined to be about 0.3 for dissolved solids and between 0.3 and 0.5 for nitrate.

Serial correlations of this magnitude indicate a tendency for subsequent values to be positively correlated to previous values. As a result, the trends determined from the regression analyses may not be as strong as indicated. Positive autocorrelations of this magnitude, however, will not significantly affect the conclusions of the temporal study.

The equations describing the average temporal changes for the hydrochemical facies were transformed back to concentrations by destandardizing the regression equations. For each hydrochemical facies, the average of the means and standard deviations of the individual wells was calculated. By multiplying the regression equations by these average standard deviations and adding the average means, equations were obtained that give the average trend in a facies in terms of concentrations. This equation describes what might be observed in a typical well in each facies, and no individual well can be expected to show the same relation.

The equations produced by this analysis are not predictive equations, but merely reflect the average rate of change over the period of record, from about 1955 to 1977. An example of the problems that can arise if they are used as predictive equations is demonstrated by considering what happens if some of the equations are used to estimate past concentrations. The equation describing the average changes in nitrate-nitrogen concentrations for the Victor Plain hydrochemical facies indicates negative concentrations in the ground water prior to 1939. This is a physical impossibility and arises because the equation was used for a purpose for which it was not intended. While predictions of future concentrations of dissolved solids and nitrate-nitrogen may not produce negative results, the values obtained could be just as meaningless.

In addition to testing for average trends throughout a hydrochemical facies, individual wells were examined for temporal variations. Where a significant trend was noted for an individual well, the equation was recorded and the well's location plotted on a map of the valley with a symbol indicating the direction of the trend (pl. 2).

Few wells in the valley have multiple observations over time. To minimize the effects of random fluctuations, only wells with seven or more observations for dissolved solids and six or more observations for nitrate were used. There was no attempt to assure a random distribution of wells throughout the valley, and all wells in the valley or along the margins having a sufficient number of observations were used. Time is measured as the year minus 1900. For example, for the year 1975, time is equal to 1975–1900 or 75.

DISSOLVED SOLIDS

Dissolved solids is a measure of the total amount of dissolved chemicals in water. An increase in any of the individual constituents will be reflected by an increase in the dissolved solids. While not many historical dissolved-solids measurements are available, many specific-conductance measurements have been made. Specific conductance is proportional to the quantity and valence of ionized chemicals in a water. Because almost all the major dissolved chemical constituents in a water are ionized, dissolved solids and specific conductance are closely related.

It was felt that dissolved solids would have more meaning for most users of this report; therefore, specific conductivities were transformed to dissolved-solids concentrations. The relation between dissolved solids and specific conductance will depend on the specific ionized species present and the amount of uncharged species, mainly silica, present in the water. For this reason, separate equations were derived for different parts of the valley. These areas do not exactly coincide with the hydrochemical facies as they were finally defined, but the division follows the same basic pattern. Thus, the effects of different water chemistries on the relation between dissolved solids and conductance were taken into account during the transformation.

Equations that describe the relation between dissolved solids and specific conductance were derived from a linear regression on data from about 650 wells having measurements of both dissolved solids and conductance. A linear equation with both slope and intercept terms was used rather than a ratio. The intercept terms of all the linear equations were significantly different from zero, which indicates that the linear equations better fit the data than ratios.

Because the calculation of dissolved solids from conductance is a simple linear transformation, the calculation in no way affects the presence of trends in the data. All dissolved-solids values for a well were estimated from conductance measurements even if some measured dissolved-solids concentrations were available. This prevented any changes that might be induced by using dissolved-solids data from different sources.

Locations of wells examined for trends in dissolved solids are shown on plate 2*A*. The changes for each hydrochemical facies are discussed in the next section and coefficients for the equations describing the average temporal changes are given in table 5. Coefficients for individual wells are summarized in table 6.

HYDROCHEMICAL FACIES

Dissolved solids in the Tuscan volcanic rocks hydrochemical facies show an average annual increase of 0.95 mg/L. The trend line accounts for 31 percent of the variation in the standardized dissolved-solids data averaged over all wells by year. A plot of the trend line is shown in figure 6. Temporal variations are significant in five of the 19 wells for which historical data are available (table 6). Two of these wells show rising trends and three show decreasing trends.

TABLE 5.—*Analyses of variance and coefficients for the regression of average yearly dissolved solids with time for the six hydrochemical facies in the Sacramento Valley*

[t=(year–1900); for example, t=(1980–1900)=80. NS, linear trend not significant at the 90 percent confidence level]

								MODEL Dissolved solids=A+B*t*			
Hydrochemical facies	Number of wells	Source	Degrees of freedom	Sum of squares	*F* ratio	Probability of exceeding *F* ratio	r^2	A	90 percent confidence limit	B	90 percent confidence limit
Tuscan volcanic rocks	19	Model	1	1.52	8.89	0.01	0.31	194	±36	0.95	±0.55
		Error	20	3.43							
		Total	21	4.95							
Victor Plain	20	Model	1	2.50	13.91	<0.01	.38	236	±48	1.61	±0.74
		Error	23	4.13							
		Total	24	6.63							
Butte Basin	12	Model	1	1.17	12.55	<0.01	.41	197	±45	1.37	±0.67
		Error	18	1.68							
		Total	19	2.85							
Sutter Basin Basin	10	Model	1	.03	.05	.83	.00	---	---	NS	---
		Error	23	15.21							
		Total	24	15.24							
North alluvial fans	62	Model	1	1.05	14.11	<0.01	.43	222	±31	1.02	±.46
		Error	19	1.41							
		Total	20	2.46							
South alluvial fans	18	Model	1	7.41	65.16	<0.01	.76	184	±67	4.75	±1.01
		Error	21	2.39							
		Total	22	9.80							

TABLE 6.—*Wells showing significant trends in dissolved-solids concentration*

[For the model: Dissolved solids=A+Bt, where t is the year minus 1900]

Well	A	Standard error	Student's *t*	B	Standard error	Student's *t*	Probability of exceeding t for B
TUSCAN VOLCANIC ROCKS							
23N/01W–09L01M	–24.6	73.2	0.34	5.72	1.12	5.12	<0.01
25N/02W–16P01M	666.4	174.5	3.82	–6.09	2.42	2.52	.01
26N/02W–09E01M	909.5	257.0	3.54	–7.44	3.56	2.09	.04
27N/03W–15N01M	1055.6	288.1	3.66	–9.56	3.92	2.44	.02
27N/03W–22B01M	–122.4	223.1	.55	6.30	3.06	2.06	.04
VICTOR PLAIN							
06N/07E–23A01M	892.6	373.4	2.39	–10.32	5.61	1.84	0.07
18N/04E–28M01M	325.8	209.4	1.56	22.03	3.02	7.29	.01
BUTTE BASIN							
16N/04E–09D01M	–389.3	181.4	2.15	8.57	2.80	3.06	<0.01
17N/01W–30K03M	1833.2	515.4	3.56	–21.27	7.04	3.02	<0.01
SUTTER BASIN							
15N/03E–15H04M	–910.0	485.4	1.87	20.92	6.82	3.07	<0.01
16N/02W–25B02M	2428.1	395.1	6.15	–24.98	5.56	4.49	<0.01
NORTH ALLUVIAL FANS							
17N/03W–33R01M	383.2	76.6	5.01	3.24	1.13	2.87	<0.01
18N/02W–01E01M	–716.6	77.8	9.21	16.37	1.16	14.16	<0.01
18N/04W–02F01M	–817.1	112.5	7.26	22.73	1.74	13.07	<0.01
19N/02W–23N01M	–464.2	77.8	5.97	14.03	1.16	12.14	<0.01
20N/02W–22E01M	–618.4	442.7	1.40	11.31	5.97	1.89	.06
21N/02W–15C01M	–241.0	84.5	2.85	8.77	1.25	7.04	<0.01
21N/03W–02Q01M	–121.4	84.6	1.43	7.41	1.25	5.95	<0.01
22N/01W–29C01M	40.2	87.8	.46	3.98	1.30	3.06	<0.01
22N/02W–03A01M	125.3	77.8	1.61	3.37	1.16	2.91	<0.01
22N/02W–04C02M	–459.7	376.8	1.22	10.53	5.11	2.06	.04
22N/03W–06H01M	–922.3	553.3	1.67	20.71	7.62	2.72	<0.01
22N/03W–22Q01M	20.0	77.8	.26	3.88	1.16	3.35	<0.01
23N/03W–35B01M	–69.5	84.3	.82	3.40	1.25	2.73	<0.01
24N/03W–24P01M	–724.6	364.0	1.99	16.36	4.95	3.30	<0.01
25N/03W–31R01M	89.9	77.8	1.16	3.49	1.16	3.02	<0.01
SOUTH ALLUVIAL FANS							
06N/01E–19L02M	–661.9	209.8	3.15	18.11	3.15	5.76	<0.01
06N/01E–19Q01M	101.0	207.1	.49	5.94	3.05	1.95	.05
06N/01W–01B04M	–166.4	280.1	.59	7.48	4.04	1.85	.07
07N/02E–34C02M	–152.3	185.0	.82	10.56	2.81	3.75	<0.01
09N/04E–33L01M	–740.0	169.8	4.36	28.96	2.75	10.55	<0.01
13N/01W–07A01M	335.8	139.7	2.40	7.43	2.04	3.64	<0.01
13N/01W–36Q02M	–32.3	117.0	.28	4.67	1.74	2.68	<0.01
14N/03W–11H01M	7.9	166.3	.05	4.45	2.46	1.81	.07

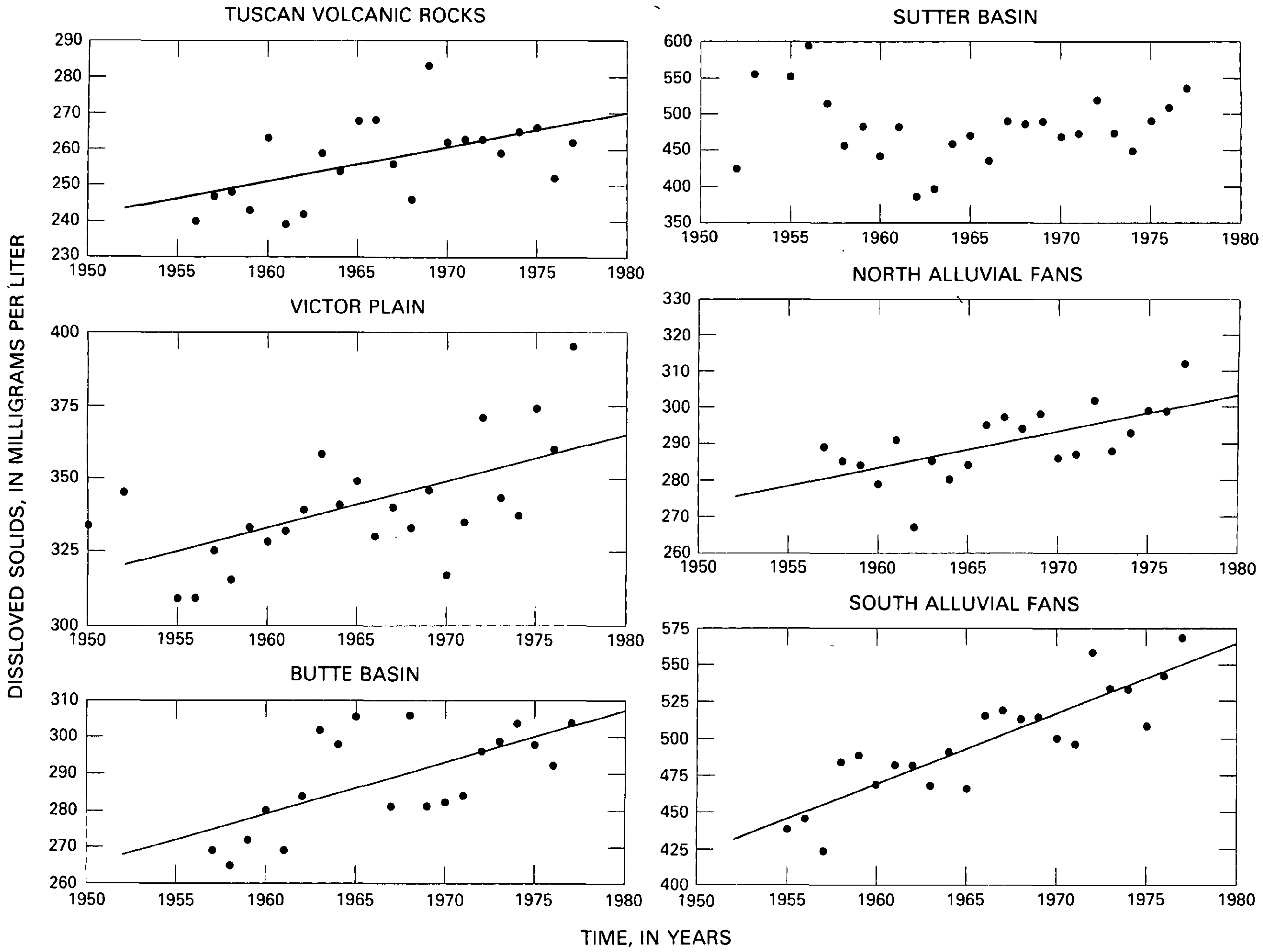

FIGURE 6.—Average yearly dissolved-solids concentrations versus time for the six hydrochemical facies in the Sacramento Valley. The coefficients and significance tests for the trend lines are given in table 5. If no line is shown, then the slope of the trend line is not significantly different from zero at the 90 percent confidence level. The technique by which the average yearly dissolved-solids values were derived is explained in the text.

The average yearly increase in dissolved solids for the Victor Plain facies is 1.61 mg/L. The trend line, which explains 38 percent of the variation in the standardized data, is shown in figure 6. Only two of the 20 wells studied in this facies showed significant changes, one of which showed an increase, and the other a decrease with time.

For Butte Basin, a temporal trend having a slope of 1.37 (mg/L)/yr explains 41 percent of the variation in the averaged data. In this facies also, two wells showed significant trends. One well demonstrated an increase and the other a decrease in dissolved solids with time.

Sutter Basin is the only hydrochemical facies to show no significant temporal change in average dissolved-solids concentration. Two of the 10 wells did show significant trends, but in opposite directions.

An increase in the average dissolved-solids concentration of the north alluvial fans facies of 1.02 (mg/L)/yr explains 43 percent of the variation in the yearly average data. A plot of the trend line is shown in figure 6. Of 62 wells that have seven or more observations in this area, 15 show significant upward trends, and none decrease.

Seventy-six percent of the variation in the average yearly dissolved-solids data are explained by a linear trend in the south alluvial fans facies. The slope is very steep 4.75 (mg/L)/yr and indicates a very rapid increase in dissolved solids (fig. 6). Of the 18 wells examined in this facies, 8 had significant increases in dissolved solids. There were no wells that showed decreases.

NITRATE

A certain amount of nitrate is present in precipitation, and chemical reactions in the soil zone may add to this amount. Thus, even under natural conditions, a finite amount of nitrate will exist in ground water. An estimate of natural nitrate concentrations in the Sacramento Valley can be made from data gathered during the period 1912–13 (Bryan, 1923). The median nitrate-nitrogen concentration in these 43 samples is 0.67 mg/L. The highest nitrate-nitrogen concentration measured was 14 mg/L, which suggests some wells were polluted as long as 70 years ago. From the frequency histogram of the 1912–13 nitrate data (fig. 7), it is estimated that under natural conditions, no more than about 3 mg/L nitrate-nitrogen would be expected in the ground water.

By the period 1974–78, the median nitrate-nitrogen concentration had more than doubled to 1.6 mg/L. The maximum observed nitrate-nitrogen concentration also increased, with two wells containing 27 mg/L and one well 61 mg/L. These increases likely reflect the influences of man's activities, and the extent of temporal changes was, therefore, investigated to determine the magnitude of the problem.

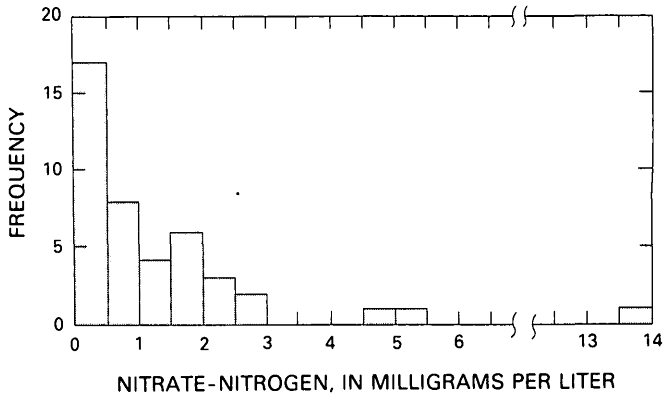

FIGURE 7.—Frequency histogram of dissolved nitrate-nitrogen concentrations in wells, 1912–13. Data from Bryan (1923).

Locations of wells examined for trends in nitrate are shown on plate 2*B*. The changes for each hydrochemical facies are discussed further and coefficients for the equations describing the average temporal changes are given in table 7. Coefficients for individual wells are summarized in table 8.

TABLE 7.—*Analyses of variance and coefficients for the regression of average yearly nitrate-nitrogen concentrations with time for the six hydrochemical facies in the Sacramento Valley*

[t=(year–1900); for example, t=(1980–1900)=80. NS, linear trend not significant at the 90 percent confidence level]

								MODEL Nitrate nitrogen=A+Bt			
Hydrochemical facies	Number of wells	Source	Degrees of freedom	Sum of squares	*F* ratio	Probability of exceeding *F* ratio	r^2	A	90 percent confidence limit	B	90 percent confidence limit
Tuscan volcanic rocks	5	Model	1	0.88	1.25	0.28	0.08	---	---	NS	---
		Error	15	10.57							
		Total	16	11.45							
Victor Plain	13	Model	1	6.05	29.31	<0.01	.63	–1.402	±0.751	0.036	±0.012
		Error	17	3.51							
		Total	18	9.56							
Butte Basin	3	Model	1	.69	1.85	.20	.12	---	---	NS	---
		Error	14	5.26							
		Total	15	5.95							
Sutter Basin	2	Model	1	.65	.84	.38	.08	---	---	NS	---
		Error	10	7.77							
		Total	11	8.42							
North alluvial fans	26	Model	1	5.02	49.67	<0.01	.73	–3.786	±1.625	.099	±0.024
		Error	18	1.82							
		Total	19	6.84							
South alluvial fans	13	Model	1	2.03	7.72	.01	.30	–0.506	±1.514	.036	±0.023
		Error	18	4.73							
		Total	19	6.76							

TABLE 8.—*Wells showing significant trends in nitrate-nitrogen concentration*

[For the model: Nitrate-nitrogen=A+Bt, where t is the year minus 1900]

Well	A	Standard error	Student's *t*	B	Standard error	Student's *t*	Probability of exceeding t for B
TUSCAN VOLCANIC ROCKS							
23N/01W–09L01M	–25.33	3.82	6.63	0.53	0.06	8.78	<0.01
25N/02W–07K01M	–7.96	3.74	2.13	.17	.06	2.89	<0.01
VICTOR PLAIN							
10N/05E–06M02M	–6.58	1.62	4.06	0.12	0.03	4.85	<0.01
11N/06E–16M01M	–9.38	1.35	6.96	.18	.02	8.56	<0.01
13N/05E–13D01M	–3.98	2.09	1.90	.08	.03	2.31	.02
14N/05E–32R03M	–14.48	2.19	6.60	.23	.03	7.38	<0.01
18N/04E–07A01M	–0.81	1.09	.75	.03	.02	1.87	.06
BUTTE BASIN							
None							
SUTTER BASIN							
None							
NORTH ALLUVIAL FANS							
18N/04W–02F01M	–73.57	6.37	11.54	1.38	0.10	13.96	<0.01
20N/03W–02D01M	–11.39	7.49	1.52	.23	.12	1.95	.05
21N/02W–15C01M	–15.47	5.62	2.75	.29	.08	3.43	<0.01
21N/03W–02Q01M	–33.53	7.80	4.30	.58	.12	4.89	<0.01
22N/01W–29C01M	–8.35	6.41	1.30	.17	.10	1.70	.09
22N/02W–03A01M	–10.26	6.16	1.67	.28	.10	2.92	<0.01
25N/03W–31R01M	–10.34	6.88	1.50	.24	.10	2.30	.02
SOUTH ALLUVIAL FANS							
09N/02E–10D01M	26.38	6.93	3.81	–0.38	0.11	3.44	<0.01
13N/01W–07A01M	–10.19	2.66	3.84	.21	.04	5.26	<.01
13N/01W–08B01M	–11.80	2.36	5.00	.22	.04	6.13	<.01
14N/03W–11H01M	–4.40	2.75	1.60	.10	.04	2.33	.02
14N/03W–14Q02M	–25.22	5.95	4.24	.38	.08	4.55	<.01

HYDROCHEMICAL FACIES

No significant average trend was found for the Tuscan volcanic rocks hydrochemical facies. However, two of the five wells examined did show significant upward trends in nitrate concentrations.

A linear trend with a slope of 0.036 (mg/L)/yr explains 63 percent of the temporal variation in the average yearly nitrate-nitrogen concentrations in the Victor Plain facies. A plot of this trend line is shown in figure 8. Of 13 wells in this area that had 6 or more observations, 5 showed significiant upward trends. None of the wells showed a significant decrease.

Neither Butte nor Sutter Basin had a significant average trend in nitrate. Also, there were no individual wells in either that showed any significant changes. However, with only three wells in Butte Basin and two in Sutter Basin having six or more observations, there are too few samples for the results of the test to be conclusive.

The nitrate-nitrogen concentrations in the north alluvial fans hydrochemical facies show a distinct upwards

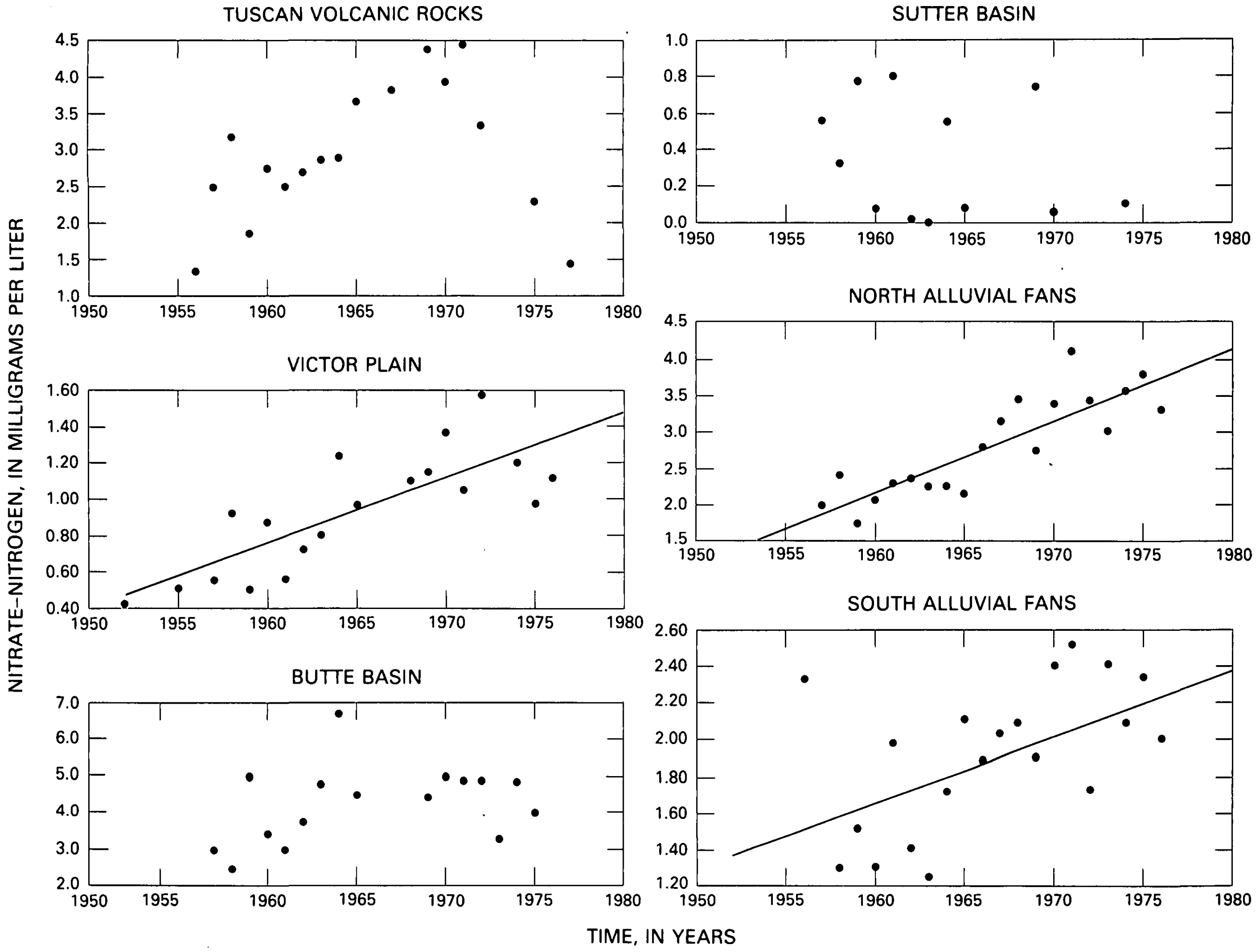

FIGURE 8.—Average yearly nitrate-nitrogen concentrations versus time for the six hydrochemical facies in the Sacramento Valley. The coefficients and significance tests for the trend lines are given in table 7. If no line is shown, then the slope of the trend line is not significantly different from zero at the 90 percent confidence level. The technique by which the average yearly nitrate-nitrogen values were derived is explained in the text.

trend with a slope of 0.099 (mg/L)/yr. Seven of the 26 wells in this facies showed significant upwards trends. The plot of the trend in figure 8 shows that the average concentration of nitrate-nitrogen in this facies has exceeded 3.0 mg/L, the maximum expected under natural conditions.

For the south alluvial fans hydrochemical facies, a linear trend having a slope of 0.036 (mg/L)/yr explains 30 percent of the temporal variation in the average annual nitrate-nitrogen concentrations. Thirteen wells had six or more observations over time, and 5 of them show significant temporal changes. Four have upwards trends, and 1 a downwards trend.

HYPOTHESIS TESTING

Because trends in the data for the individual wells were tested at the 90 percent confidence level, there is a 10 percent chance that no significant trend exists in the valley. The significant slopes that were observed could result from normally distributed random fluctuations about a true true slope of zero. If this were the case, 5 percent of the wells could show a significant increase, and 5 percent a significant decrease, although no real trend existed. If more than 5 percent of the dissolved-solids or nitrate wells show significant trends in the same direction, then it can be concluded that there has been a significant change for that species.

Of 140 wells in the Sacramento Valley tested for trends in dissolved solids, 28 (20 percent) showed an increase and 7 (5 percent) showed a decrease with time. Under the null hypothesis that no change in dissolved solids is occurring at the 90 percent confidence level, it would be expected that by random variation, 7 of the wells would show a significant decrease and 7 would show a significant increase. For dissolved solids, the number of wells showing increases exceeds the number expected by random variation, and the increase in dissolved solids is significant.

Of 62 wells tested for trends in nitrate, 18 (29 percent) showed increases, but only 1 (2 percent) showed a decrease with time. Under the null hypothesis of no change, 3 can be expected to increase and 3 to decrease by random variation at the 90 percent confidence level. Because 29 percent of the wells showed significant increases in nitrate, the null hypothesis can be rejected, which indicates significant increases in nitrate are occurring in the Sacramento Valley.

PROCESSES CONTROLLING GROUND-WATER CHEMISTRY

Differences in the chemical composition of ground water among the six hydrochemical facies in the Sacramento Valley indicate that either different processes control the water chemistry in different areas, or that there are spatial variations in the same process. In this section, the major controlling processes are delineated from the chemical data using principal components analysis. Factor scores are than calculated for each well that reflect the magnitude of each component in that well. By studying the spatial trends in the factor scores using trend surface analysis, the areal variations in processes can be determined. Contour maps of these surfaces show the spatial distributions of the more important processes controlling ground-water chemistry.

METHODS OF DATA ANALYSIS

PRINCIPAL COMPONENTS ANALYSIS

Principal components analysis (Rummel, 1970; Davis, 1973) is used to separate the variance of a data matrix into common and unique components. Variables, in this case dissolved chemical species, that are controlled by the same process will share a common variance structure. Principal components analysis will group the variables on the basis of this shared variation and will calculate a correlation between variables and components. These components represent independent sources of variation in a data matrix and can be interpreted in terms of controlling processes using knowledge of geochemical principles.

From the correlations, or loadings as they are termed, between variables and components, factor scores can be calculated for each well that measure the intensity of a component in that well. These factor scores are a composite of all the chemical species that load on a component and summarize similar behavior in a number of different species. Where several of the chemical species are controlled by the same process, this transformation to factor scores reduces the number of variables needed to account for the significant variation in the data. The factor scores can be further analyzed as any other numerical variable.

TREND SURFACE ANALYSIS

Trend surface analysis (Davis, 1973) is a technique for separating variation in geographically distributed data into regional and local parts. Either of these parts might be the goal of a particular study. For the distribution of processes in the Sacramento Valley, however, the regional variation is of interest. A trend surface is delineated by a polynomial equation that predicts the magnitude of some variable in terms of the geographic coordinates of a set of observations. The criteria for fitting the polynomial is to minimize the squared deviations about the surface. In this study, the trend surface represents the spatial variation in processes controlling ground-water chemistry. By contouring the surface, maps can be prepared that show the spatial variation in the magnitude of the process.

PROCESSES AND THEIR SPATIAL VARIATION

For the Sacramento Valley, 15 variables (table 9) were included in the principal components analysis. A major assumption of components analysis is that the data are normally distributed. This requirement was reasonably well met by using logarithmic transformations of the chemical concentrations. Four principal components explained 73 percent of the total variation in the data and accounted for all the significant common variation (that is, only these four components had eigenvalues greater than one). The four individual components explained 36, 17, 11, and 9 percent of the total variation. Because neither the third nor fourth component yielded clear interpretations that could be attributed to processes, only the first two components are presented. These two components, however, explain

TABLE 9.—*Chemical variables included in the principal components analysis of the Sacramento Valley*

Dissolved solids	Potassium	Silica	Nitrate
Calcium	Manganese	Bicarbonate	Phosphate
Magnesium	Arsenic	Sulfate	Fluoride
Sodium	Boron	Chloride	

TABLE 10.—*Results of principal components analysis on chemical data from the Sacramento Valley*

[All loadings with absolute values less than 0.30 have been omitted for clarity]

	Components		Communalities
	1	2	
Dissolved solids	0.94		0.93
Calcium	.76		.60
Magnesium	.81		.67
Sodium	.83		.76
Bicarbonate	.85		.72
Chloride	.76		.62
Sulfate	.63		.41
Boron	.65		.42
Fluoride	.30	–0.46	.30
Silica	–0.54	.42	.46
Potassium		.67	.48
Nitrate		–0.71	.52
Phosphate		.50	.30
Manganese		.63	.41
Arsenic		.62	.38
Percent variation explained	36	17	
Cumulative percent variation explained	36	53	

over 50 percent of the variation in the chemical data from the Sacramento Valley.

Table 10 shows the results of the principal components analysis. On component one, dissolved solids, calcium, magnesium, sodium, bicarbonate, chloride, sulfate, boron, and fluoride all have positive loadings. Silica is the only species to have a significant negative loading on this component. The inverse loadings of dissolved solids and silica indicate that low silica concentrations tend to be found in conjunction with high dissolved-solids concentrations, and vice versa. The positive loadings of all the major chemical species on this factor indicate a source high in calcium, magnesium, sodium, bicarbonate, chloride, and sulfate. This source is also high in fluoride and boron, and low in silica.

The trend surface map of this component (fig. 9) shows a distinct linear trend across the valley, which accounts for 36 percent of the spatial variation in component one. Low values of component one along the eastern margin and in the northern end of the valley indicate low dissolved-solids and high silica concentrations. In the southwestern corner, high concentrations of dissolved species and boron are indicated. This distribution in the ground water is very similar to the distribution of water chemistry in surface streams draining into the valley. Table 11 shows the average concentrations of dissolved species in streams entering the valley from certain areas. East side streams are low in dissolved solids, and contain twice as much silica as streams from the southwestern margin. The silica in east side streams is likely from the weathering of volcanic detritus in the Sierra Nevada and Cascade Range. High dissolved-solids concentrations in the southwest originate in thermal springs in the Coast Ranges.

The first principal component represents the effects of the chemistry of recharge to the valley on the chemistry of the ground water. This process is active along both margins of the valley and produces fairly uniform chemical compositions along the eastern side. Along the western margin, changes in surface-water chemistry from north to south induce changes in ground-water chemistry. The effects of recharge chemistry are the single most important control on ground-water chemistry, accounting for over one-third of the total variation in the chemical data.

The second principal component (table 10) explains 17 percent of the variation in the chemical data, and contains positive loadings of silica, potassium, phosphate, manganese, and arsenic. Nitrate and fluoride have negative loadings on this component. The trend surface for component two (fig. 10) explains 38 percent of the spatial variation in this component. The pattern indicates high factor scores in the center of the valley with low values along the margins. The occurrence of high factor scores in wells in the flood basins suggests that the fine-grained sediments and reducing conditions in the basins are an important control on water chemistry.

Measurements of dissolved oxygen in the ground water in the south alluvial fans facies (table 12) show an average of 3.8 mg/L of dissolved oxygen. Although no data are available for other parts of the valley, it is reasonable to assume that the coarse-grained sediments along the valley margins would contain some dissolved oxygen. In the flood basins, where sediments are water saturated and fine grained, reducing conditions probably exist. The increase in manganese and arsenic, and decrease in nitrate, support an oxidation-reduction effect. The solubility of manganese and arsenic increases in reducing conditions, and nitrate could be removed by denitrification.

Longer residence times in the fine-grained sediments of the flood basins and weathering of volcanic detritus from Sutter Buttes could supply the higher silica and potassium concentrations indicated by component two. The inverse relation between phosphate and fluoride probably reflects spatial differences in their sources rather than equilibrium with a mineral phase, such as apatite. Phosphate, introduced along with nitrate, would not be removed by reduction reactions and would persist in the ground water. Fluoride is probably derived from thermal springs in the hills surrounding the valley and lacks a source in the central basins.

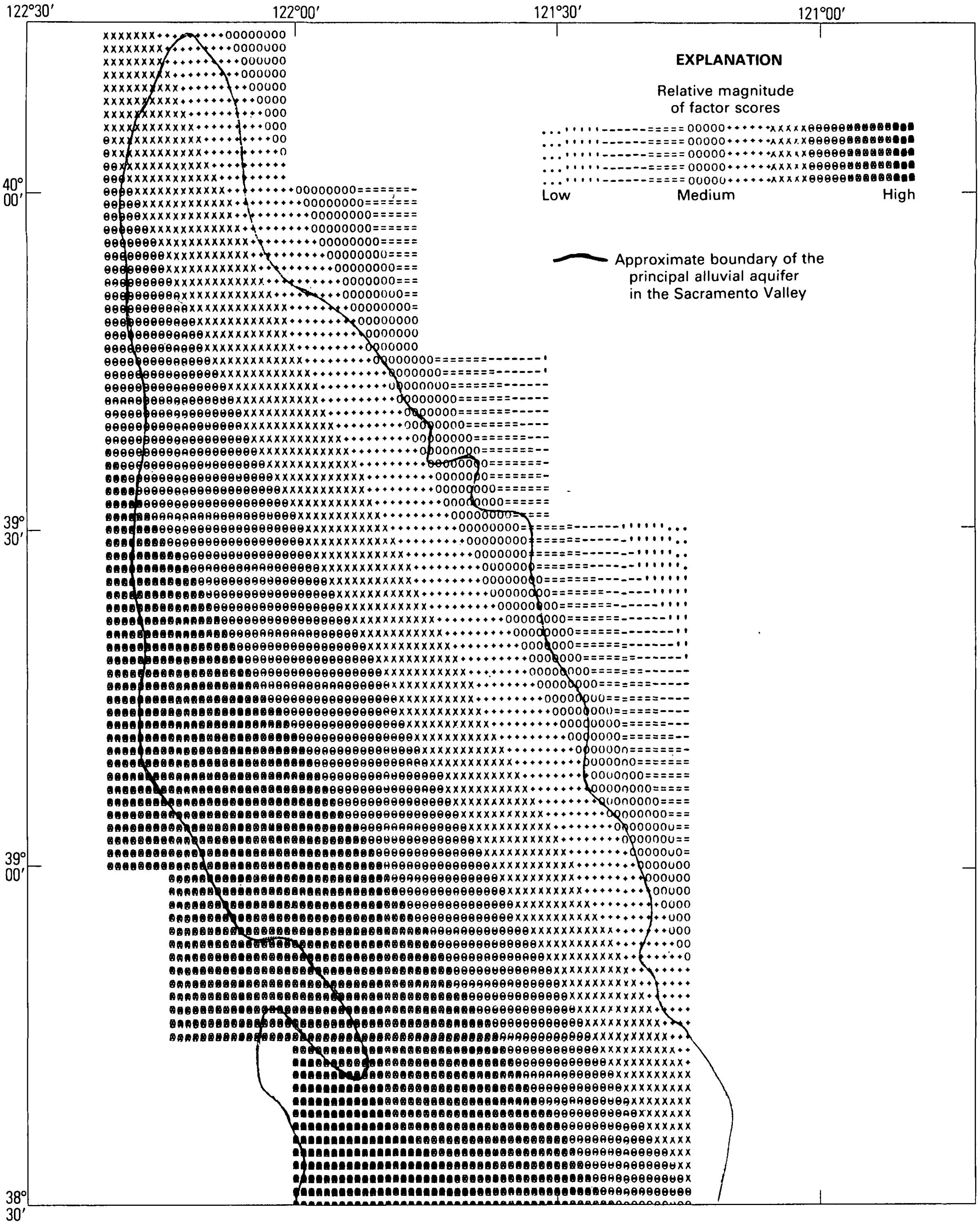

FIGURE 9.—Trend surface of factor scores for component one.

Principal components analysis shows that two components account for over 50 percent of the variation in the chemical data from the Sacramento Valley. While other processes will affect water chemistry, they seem to be either more localized or much less important than the two discussed. Recharge from the valley margins

TABLE 11.—*Average chemical compositions of surface water entering the Sacramento Valley*

Species (mg/L)	East side	Northern west side	Southern west side
Dissolved solids	85	215	592
Calcium	11	36	53
Magnesium	4.7	12	40
Sodium	6.3	13	101
Bicarbonate	55	164	314
Chloride	5.4	16	150
Sulfate	7.0	28	82
Boron	.10	.07	.51
Fluoride	.08	.08	.4
Silica	22	14	11

EXPLANATION OF LOCALITIES

East side: Antelope Creek, Mill Creek, Big Chico Creek, Butte Creek, Feather River, Yuba River, Bear River, and American River.

Northern west side: Red Bank Creek, Elder Creek, Thomes Creek, and Stony Creek.

Southern west side: Stone Corral Creek, Lurline Creek, Freshwater Creek, Salt Creek (west of Williams), Cortina Creek, Sand Creek, Oat Creek, Cache Creek, and Putah Creek.

is the most important control on ground-water chemistry, with reactions in the flood basin sediments also being important.

MINERAL STABILITY RELATIONS

Sediments deposited in the Sacramento Valley have been derived from erosion of the surrounding mountains. These mountains contain igneous and metamorphic rocks which were formed at higher temperatures and (or) pressures than are found at shallow depths in the valley sediments. Because the environment of deposition is radically different from that of formation, these minerals are generally not in equilibrium with their surroundings. As a result, the minerals react with the ground water, which dissolves the unstable primary minerals and forms secondary minerals that are more stable. Reaction rates may be very slow, so the process is gradual and can take tens of millions of years or longer. During this diagenesis, phases, such as pyroxenes, feldspars, micas, and volcanic glass, weather to more stable phases, such as clay minerals and iron hydroxides.

Water chemistry will be affected by water-rock interactions, and the three parts of the system (primary minerals, aqueous solution, and secondary minerals) are interdependent. Using thermodynamic calculations, the mineral phases that will be stable in equilibrium with solutions of various compositions can be predicted. It cannot be justifiably presumed, however, that the mineral assemblage and the ground-water chemistry are in thermodynamic equilibrium, particularly where aluminosilicate minerals are involved. Water chemistry may reflect incomplete reactions or partial equilibrium with metastable phases.

In this section, the relations between water chemistry and aquifer mineralogy are examined. Mineralogy is presented from two U.S. Geological Survey test wells. Mineral saturation indices are examined to determine any likely phases that may be controlling water chemistry. Finally, stability and metastability fields of mineral phases are compared to measured water chemistry to determine what secondary minerals will be most stable in contact with Sacramento Valley ground water.

MINERALOGY OF SEDIMENTS

Sidewall samples were collected from various depths in two test wells drilled by the U.S. Geological Survey during 1979. Data from two wells do not provide a comprehensive evaluation of sediment mineralogy, but they do provide a partial guide to what minerals may be present. Not all the samples have been analyzed as of the time of this writing and additional mineralogic data will be published in the future as basic data reports.

WELL 12N/01E–34Q

The mineralogy of sidewall samples from well 12N/01E–34Q was determined by optical microscope identification of the 0.5- to 0.125-mm size fraction. Table 13 shows the percent compositions of minerals, in this size range, for five samples collected from 323 feet to 897 feet. Data from an additional sample at 1,845 feet is also given. Feldspars compose an average of about two-thirds of the mineral grains, with about one-fifth being quartz and one-tenth being rock fragments. In all the shallower samples, the percent plagioclase having an anorthite content greater than 34 percent is smaller in the fine fraction than in the medium. The sample from 1,845 feet has an unusually small amount of anorthite-rich plagioclase in the medium fraction. The albitic plagioclase component increases between medium and fine fractions in all but one sample. The smaller size fractions, which are chemically more reactive, are dominated by albitic plagioclase.

Lithic fragments from a gravel at 1,856 feet, having a distinct greenish hue, were examined by X-ray diffraction. The sample near this depth was unusually rich in heavy lithic fragments (table 13). X-ray analysis of these fragments indicates that the composition is quartz, plagioclase, and chlorite (Ivan Barnes, U.S. Geological Survey, personal commun., 1979). The mineralogy of the sediments determined by optical methods may not reflect the complete mineralogy, especially where some minerals are contained in rock fragments which are not differentiated mineralogically. Mineral phases identified in samples from this well are shown in table 14.

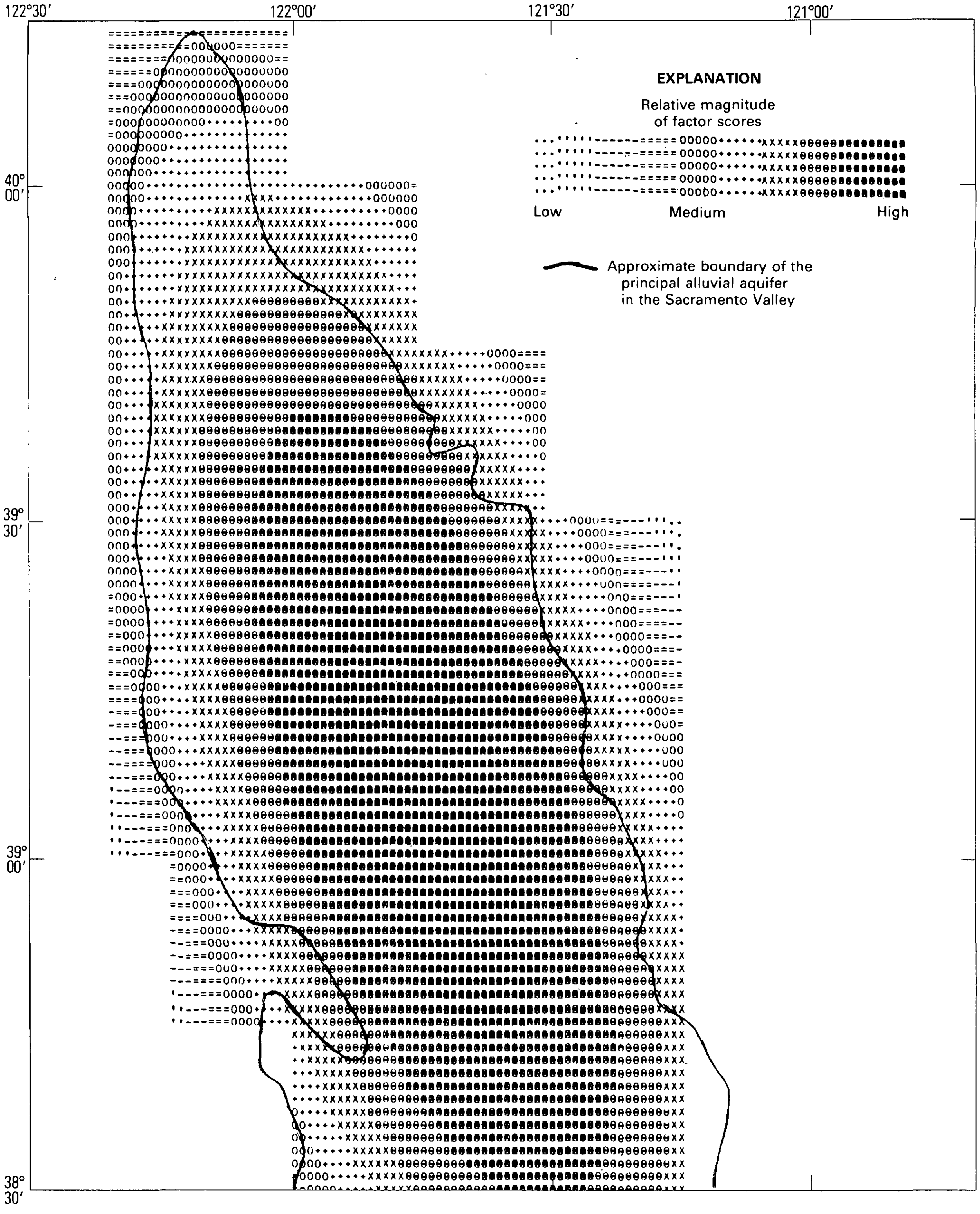

FIGURE 10.—Trend surface of factor scores for component two.

WELL 19N/01W–32G

The mineralogy of a number of fine-grained layers was determined by X-ray diffraction analysis of sidewall samples from well 19N/01W–32G. The results of the analyses are shown in table 15. Below a depth of about 562 feet, a large component of X-ray amorphous material is present in the sediments. Whether this is primary volcanic glass or an intermediate weathering

TABLE 12.—*Dissolved-oxygen concentrations in well water in the south alluvial fans facies*

Well	Date	Dissolved oxygen (mg/L)
08N/03E–05N04M	08–01–79	1.9
08N/03E–06M01M	08–01–79	2.0
08N/01E–06B01M	07–31–79	5.9
08N/01E–17C01M	07–26–79	5.0
09N/03E–31L01M	08–01–79	2.0
09N/02E–18N01M	07–31–79	4.4
09N/02E–33E01M	07–31–79	7.8
09N/01E–35H02M	07–31–79	3.8
09N/01W–25M01M	07–31–79	3.2
10N/02E–03E01M	07–25–79	2.8
11N/01W–01D01M	07–25–79	3.5
Mean		3.8

product, such as an amorphous aluminosilicate (Paces, 1978) was not investigated. The two clay minerals present in quantity are halloysite and illite. The presence of halloysite rather than kaolinite was determined using transmission electron microscopy. Figure 11 shows an electron micrograph of sediments from the 407-foot depth. The tubular structures at the center and top of the figure are halloysite, with poorly formed flakes of illite also visible. The dark, blocky particles are fine-grained quartz and plagioclase.

Optical examination of sand-size grains shows that the mineralogy is consistent with an andesitic sand. The major mineral is plagioclase, which is zoned and shows etching. Some pyroxenes are present and are clear to light green. Many of the grains are stained by ferric hydroxides.

SATURATION INDICES

According to the law of mass action, when an aqueous solution is in equilibrium with a mineral, the ion-activity product for that mineral will equal the thermodynamic equilibrium constant. The degree of saturation of a water can be represented by the saturation index (*SI*), which is the logarithm of the quotient of the ion-activity product (*IAP*) divided by the equilibrium constant (*K*):

$$SI=\mathrm{Log}\,\frac{IAP}{K}, \qquad (1)$$

where

SI=saturation index

IAP=ion-activity product, and

K=thermodynamic equilibrium constant.

The saturation index has a value of zero when the solution is in equilibrium with a solid phase. A positive saturation index indicates supersaturation and a negative index undersaturation with respect to some mineral. Minerals that are present in an aquifer and have negative saturation indices can dissolve. Minerals that have positive saturation indices may precipitate from solution, although whether this actually occurs depends on additional factors. By examining the saturation indices of water samples collected from the Sacramento Valley, some idea can be obtained about which minerals may be influencing ground-water chemistry.

TABLE 13.—*Mineralogic compositions of sidewall samples from U.S. Geological Survey test well 12N/01E–34Q*

c—coarse >0.5 mm.
m—medium 0.5–0.25 mm.
f—fine 0.25–0.125 mm.
vf—very fine 0.125–0.0625 mm.
p—pan <0.0625 mm.

VAB—very abundant, from 25–50 percent of the heavy minerals.
AB—abundant, from 10–25 percent of the heavy minerals.
SP—sparse, from 1–4 percent of the heavy minerals.

Sample depth, in feet	323		467		685		788		897		1845	
Texture, in percent c/m/f/vf/p	7/2/41/34/17		2/2/8/43/45		3/5/19/38/36		60/22/10/3/5		8/52/28/4/8		59/18/6/4/12	
Size interval	m	f	m	f	m	f	m	f	m	f	m	f
Composition, in percent:												
Potassium feldspar	12	13	6	16	27	13	15	14	15	12	10	12
Plagioclase (Anorthite<34)	25	44	40	33	22	32	21	36	28	39	19	24
Plagioclase (Anorthite>34)	28	10	24	14	25	16	23	12	23	14	3	13
Quartz	20	23	20	28	20	26	21	18	7	13	31	18
Lithic fragments	11	10	7	6	4	10	14	13	21	12	21	11
Heavy minerals[1]	3	1	3	3	2	2	5	6	6	13	15	23
Nonopaque heavy grains:												
Sausserite	VAB		VAB		VAB		VAB		AB		AB	
Uralite	VAB		VAB		VAB		VAB		AB		AB	
Goethite	VAB		VAB		VAB		VAB		AB		AB	
Lithic fragments	AB		SP		SP		AB		AB		VAB	

[1] Heavy minerals have specific gravities greater than 2.9.

TABLE 14.—*Minerals identified in sidewall samples from U.S. Geological Survey test well 12N/01E–34Q, in alphabetical order*

Actinolite-tremolite (series)[1]
Amphiboles
Analcite
Apatite
Augite-ferroaugite (series)[1]
Basic glass
Biotite
Bronzite-ferrohypersthene (series)[1]
Chlorite
Chromite
Chrysotile
Clinozoisite
Cordierite
Cummingtonite
Diopside-hedenbergite (series)[1]
Enstatite-bronzite (series)[1]
Epidote
Fluorite
Garnet (red)
Glauconite
Glaucophane
Graphite
Hematite (some specular)
Hercynite
Hornblende (green, brown, and oxy-varieties)
Hypersthene
Lawsonite
Marcasite
Pigeonite
Plagioclase (series)[1]
Potash feldspar (undifferentiated)
Pumpellyite
Richterite (part of series)[1]
Riebeckite
Serpentine (?)
Sideromelane
Sphene (titanite)
Spinel
Staurolite
Zircon
Zoisite

[1] "Series" means several varieties within the series were found.

TABLE 15.—*Percent mineral composition of sidewall samples from U.S. Geological Survey test well 19N/01W–32G*
[Tr, trace; unid., unidentified; inter., intermediate; ND, not detected]

Depth (feet)	Quartz	Plagioclase	Amorphous	Halloysite	Illite	Other
260	35–45	25–35	ND	15–20	5–10	Tr unid.
353	40	15–20	ND	10–15	ND	Tr minor.
407	35–40	20–25	ND	10–15	2–5	Tr minor.
478	35–40	25–30	ND	10–15	5–10	5–10 Chlorite.
562	10–20	15–25	Major	5–15	2–5	ND.
630	20–25	15–20	Inter.	5–10	2–10	Tr unid.
930	15–20	10–15	Inter.	10–15	5–10	ND.
984	5–15	5–10	Major	10–15	1–5	Tr unid.
1,098	5–10	5–10	Major	5–10	1–5	ND.
1,193	5–15	5–10	Major	5–10	1–5	Tr minor.
1,390	5–10	2–5	Major	2–5	2–5	ND.

Saturation indices were calculated for 271 water analyses selected from those published by Fogelman (1975, 1976) and Fogelman and Rockwell (1977). Of the 271, 153 had aluminum analyses and 183 had iron analyses. Temperature, pH, and alkalinity were determined in the field. Samples for cation determinations were passed through a 0.1-micrometer filter and acidified with concentrated nitric acid. Some controversy exists as to the validity of aluminum and iron data gathered in this manner; however, the possible error introduced is generally small (Kennedy and others, 1974; Barnes, 1975). Some of the supersaturation in the aluminosilicate and iron minerals may be due to particulate iron and aluminum passing through the filter. Saturation indices were calculated using WATEQF (Plummer, and others, 1978).

Table 16 shows the mean, minimum, and maximum saturation indices for selected mineral phases along with log equilibrium constants at 20°C, the average temperature of ground waters in the Sacramento Valley. Although many minerals, such as the feldspars and montmorillonite, show variations in chemical composition, saturation indices were calculated for ideal mineral phases. Therefore, stability calculations for these minerals only approximate actual conditions, but they do provide useful indicators of the types of reactions that may be occurring.

Most waters are close to saturation with respect to silicaglass, as might be expected from the volcanic detritus in the sediments. All samples were supersaturated with respect to amorphous ferric hydroxide, which may reflect the variability in solubility with particle size or particulate iron passing through the 0.1-micrometer filter during sampling. The waters tend to be at saturation with respect to gibbsite and slightly below saturation with respect to amorphous aluminum hydroxide.

Ground water is fairly close to saturation with respect to the carbonate minerals, calcite, dolomite, and magnesite. No carbonate minerals were recorded in sediments from either of the wells examined for mineralogy. Apparently, the formation of secondary carbonate minerals is of limited extent despite a number of samples indicating supersaturation with respect to calcite.

Potassium and sodium feldspars, which are abundant in the sediments, average close to saturation in Sacramento Valley ground water. Dissolution of these phases probably contributes to water chemistry where ground water is undersaturated with respect to these feldspars. All water samples are undersaturated with respect to anorthite, which is less abundant in the sediments. Halloysite is the only clay mineral with which the ground water is not supersaturated. Any of the other clay minerals could potentially form from most of the waters. When stability fields are considered, however, only one phase will be the most stable. These phase relations can be illustrated using activity diagrams.

ACTIVITY DIAGRAMS

Activity diagrams can be used to illustrate the phase relations among primary and secondary minerals and to predict the most stable secondary phases as a function of water chemistry. Such diagrams have been used by Feth, Roberson, and Polzer (1964), Tardy (1971) and White (1979) to depict weathering reactions in ground

FIGURE 11.—Electron micrograph of sediments from the 407-foot depth of well 19N/01W–32G. (Photograph by Technology of Materials, Santa Barbara, Calif.)

waters. The technique for calculating such diagrams is given in Garrels and Christ (1965), and Helgeson, Brown, and Leeper (1969) give numerous examples of such diagrams. A slightly different type of diagram, though basically similar, was presented by Kittrick (1969), and it depicts equilibrium between solid phases and an aqueous solution.

As an example of the calculation of the equilibrium boundary between two phases, the calculation of the phase boundary between illite and montmorillonite is given below. Formulas for these minerals are taken from WATEQF (Plummer, and others, 1978). For the reaction illite ⇆ montmorillonite, the chemical equation is written

TABLE 16.—*Mean, minimum, and maximum saturation indices in Sacramento Valley ground water for selected mineral phases*

Phase[1]	n	[2]Log *K* at 20 °C	Saturation index		
			Mean	Minimum	Maximum
Silica glass	271	–3.07	–0.14	–0.58	0.16
$Fe(OH)_3$ amorph.	183	4.885	1.31	.62	3.67
$Al(OH)_3$ amorph.	153	–31.77	–1.13	–2.32	.03
Gibbsite	153	–32.95	.05	–1.15	1.22
Fluorite	269	–11.02	–2.38	–3.50	–0.10
Hydroxyapatite	270	–59.57	–2.22	–7.57	1.64
Strengite	183	–26.37	–0.61	–2.06	1.05
Calcite	271	–8.45	–0.33	–1.80	.50
Dolomite	271	–16.92	–0.54	–3.37	1.24
Magnesite	271	–8.16	–0.53	–1.96	.43
Adularia	153	–20.96	.22	–1.81	1.66
Albite	153	–18.32	–0.82	–2.93	.47
Anorthite	153	–19.55	–3.27	–5.95	–1.77
Halloysite	153	–33.38	–0.89	–3.76	1.38
Kaolinite	153	–37.52	3.26	.32	5.58
Illite	153	–40.99	2.31	–1.33	4.53
Montmorillonites:					
1. Calcium	153	–45.73	3.40	–0.37	5.84
2. Belle Fouche.	95	[3]–34.97	7.49	4.04	9.01
3. Aberdeen	95	[3]–29.69	6.69	3.43	8.10
Muscovite	153	–49.94	1.35	–3.12	4.61
Chlorite	153	–91.29	–1.83	–12.11	3.52

[1] Chemical formulas for these phases are as written in WATEQF (Plummer and others, 1978.)

[2] Data from the latest version of WATEQF.

[3] The log equilibrium constant at 25°C is used because no enthalpy is given in WATEQF.

$$(K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2)+2.48H_4SiO_4 +0.52Fe^{+3}+0.45Mg^{+2} \leftrightarrows 3.13H_2O+0.6K^{+1}+1.86H^{+1} +1.56(H_{0.42}Mg_{0.46}Fe_{0.34}Al_{1.47}Si_{3.82}O_{10}(OH)_2). \quad (2)$$

At the phase boundary, the ion-activity product for this reaction will equal the equilibrium constant (*K*):

$$\frac{[K^{+1}]^{0.6}[H^{+1}]^{1.86}}{[H_4SiO_4]^{2.48}[Fe^{+3}]^{0.52}[Mg^{+2}]^{0.45}}=K. \quad (3)$$

Brackets denote free ion activities, which are concentrations corrected for the nonideality of aqueous solutions. Rewriting in terms of log activities gives the equation:

$$0.61 \log [K^{+1}]/[H^{+1}]–0.52 \log [Fe^{+3}]/[H^{+1}]^3 –0.45 \log [Mg^{+2}]/[H^{+1}]^2-2.48 \log [H_4SiO_4]=\log K. \quad (4)$$

To plot this line on a two-dimensional graph, the equation must be reduced to two variables. The assumptions that may be considered when plotting phase diagrams include (1) controlling the concentration of a component by equilibrium with a solid phase, (2) conserving a component in solid phases during phase transformations, and (3) assigning a specified concentration for a species in solution, commonly the average for that species in the study area.

In all plots below, it is assumed that the logarithm of the activity quotient of free ferric iron to hydrogen cubed ($\log [Fe^{+3}]/[H^{+1}]^3$) is controlled by the solubility of amorphous ferric hydroxide at 4.885 (Plummer and others, 1978). The average for the log activity ratio of potassium to hydrogen ($\log [K^{+1}]/[H^{+1}]$) in the valley is 2.75, and ratio of magnesium to hydrogen squared ($\log [Mg^{+2}]/[H^{+1}]^2$) is 11.25. The average log activity of silica in ground waters is -3.21. The use of these averages where a concentration must be assumed in the calculation of a phase transformation does not significantly affect the depicted relations between data points and phase boundaries in the following activity diagrams.

For the equilibrium between illite and montmorillonite, $\log [Fe\ ^{3}]/[H^{+1}]^3$ is assumed to be controlled by the solubility of ferric hydroxide, and $\log [H_4SiO_4]$ is assigned a value of -3.21. Replacing these quantities in equation 4 gives the following equation for the phase boundary between illite and montmorillonite:

$$\log [K^{+1}]/[H^{+1}]=0.122+0.743 \log [Mg^{+2}]/[H^{+1}]^2. \quad (5)$$

Two types of diagrams are presented here to illustrate phase relations in the system MgO-K_2O-Fe_2O_3-Al_2O_3-SiO_2-H_2O. The diagrams depart, to some extent, from the traditional presentation in that metastable phases are included. Recent work by Paces (1973, 1978) and Busenberg (1978) indicates that during the weathering of feldspars, the initial solids formed are amorphous to poorly crystalline aluminosilicates which may be reversible with respect to the aqueous solution. Subsequent crystallization results in the formation of a metastable aluminosilicate commonly called halloysite. Eventually, the thermodynamically most stable mineral will form. This pathway between primary and secondary minerals generally follows Ostwald's Rule (Darken and Gurry, 1953), which states that when a system is proceeding from a less to a more stable state, the final most stable state is not necessarily reached directly but may be attained through a series of intermediate states. Neither halloysite nor illite are stable with respect to montmorillonite or kaolinite, yet they are present in the sediments. Activity diagrams showing metastable states indicate the intermediate steps, as well as the final secondary minerals that are expected to form.

All minerals included in the following diagrams are from WATEQF and have formulas and log equilibrium constants from that program. Because no information is available on the chemistry of clay minerals from the Sacramento Valley, particularly illite and montmorillonite, no better substitute is available. This use of surrogate minerals will introduce some uncertainty in the exact locations of phase boundaries in the diagrams. Considering the uncertainty in the knowledge of thermodynamic data on montmorillonites and illites, it is doubtful if full knowledge of mineral chemistry would improve the situation. The montmorillonite used in all the diagrams is Aberdeen montmorillonite (Kittrick, 1971) with modifications by Truesdell and Jones (1974).

Figure 12 shows the stability fields of minerals as a function of $pH\text{-}\frac{1}{3}pAl^{+3}$ and $p[H_4SiO_4]$, where p stands for -log as in $pH=\text{-}\log [H^{+1}]$, and $pAl^{+3}=\text{-}\log [Al^{+3}]$. This diagram depicts the formation of secondary minerals from an aqueous solution. The solution, in this case, is assumed to have the average ion activity ratios and silica activity observed in the Sacramento Valley. No solid phase will form from solutions with low aluminum to hydrogen ratios and low silica concentrations (bottom right corner of figure 12). At higher aluminum to hydrogen ratios, the stable solid phase changes from gibbsite to kaolinite to montmorillonite with increasing silica. Halloysite and amorphous aluminum hydroxide phase boundaries are dashed to emphasize that they are both metastable phases. A solution in equilibrium with halloysite will be supersaturated with respect to montmorillonite or kaolinite. All samples from the valley plot in the montmorillonite stability field. Only 10 percent of the samples are supersaturated with respect to halloysite.

Regression analysis was used to determine if any significant linear relation exists between aluminum and silica. Each hydrochemical facies was treated separately to preserve as much detail as possible. Only two of the regression equations were significant, those for the Tuscan volcanic rocks and the Sutter Basin facies.

The equation for the Tuscan volcanic rocks facies is

$$pH\text{-}\tfrac{1}{3}pAl^{+3}=2.10+0.39p\,[H_4SiO_4] \qquad (6)$$

with r^2 equal to 0.26 and coefficients and their 90 percent confidence limits of

$$2.10 \pm 0.83$$

and

$$0.39 \pm 0.27.$$

Rewriting the equation in terms of log activities gives

$$0.33 \log [Al^{+3}]/[H^{+1}]^3=2.10\text{-}0.39 \log [H_4SiO_4]. \qquad (7)$$

The inverse relation between the aluminum to hydrogen ratio and silica is indicative of control by a mineral phase. As silica increases in solution, $\log [Al^{+3}]/[H^{+1}]^3$ decreases to compensate.

The slope is close to and not significantly different from 0.33. Assuming that it is 0.33 and rearranging gives

$$\frac{[Al^{+3}][H_4SiO_4]}{[H^{+1}]^3}=10^{6.31}. \qquad (8)$$

The solution of halloysite or kaolinite is given by the equation:

$$\tfrac{1}{2}Al_2Si_2O_5(OH)_4+3H^{+1} \leftrightarrows \tfrac{1}{2}H_2O+Al^{+3}+H_4SiO_4. \qquad (9)$$

The ion activity product is

$$\frac{[Al^{+3}][H_4SiO_4]}{[H^{+1}]^3}=K. \qquad (10)$$

For halloysite log K equals 6.83 and for kaolinite, 4.76. The close agreement between the ion activity product of halloysite in ground water from the Tuscan volcanic rocks facies with the equilibrium constant is strong evidence that halloysite is controlling the aluminum and silica concentrations in ground water.

The Sutter Basin hydrochemical facies also showed a significant relation between $pH\text{-}\frac{1}{3}pAl^{+3}$ and $p[H_4SiO_4]$.

$$pH\text{-}\tfrac{1}{3}pAl^{+3}=6.13\text{-}0.92p[H_4SiO_4] \qquad (11)$$

with r^2 equal to 0.27 and coefficients and their 90 percent confidence limits of

$$6.13 \pm 2.91$$

and

$$0.92 \pm 0.91.$$

Rewriting the equation in terms of log activities gives

$$0.33 \log [Al^{+3}]/[H^{+1}]^3=6.13+0.92 \log [H_4SiO_4]. \qquad (12)$$

The positive slope is indicative of solution control of water chemistry, with both aluminum and silica increasing as some mineral phase is attacked by hydrogen ion. The slope is close to and not significantly different from one. This gives an aluminum to silica ratio in the dissolving phase of 1 to 3. The most likely minerals are, therefore, potassium and sodium feldspars, which have an aluminum to silica ratio of 1 to 3. This aluminum to silica ratio, along with the etched surfaces of feldspar grains observed under the microscope, may reflect stoichiometric dissolution of feldspars as found by Holdren and Berner (1979) and Berner and Holdren (1979).

Figure 13 shows the phase stability fields for minerals in terms of the log activity ratios of magnesium to

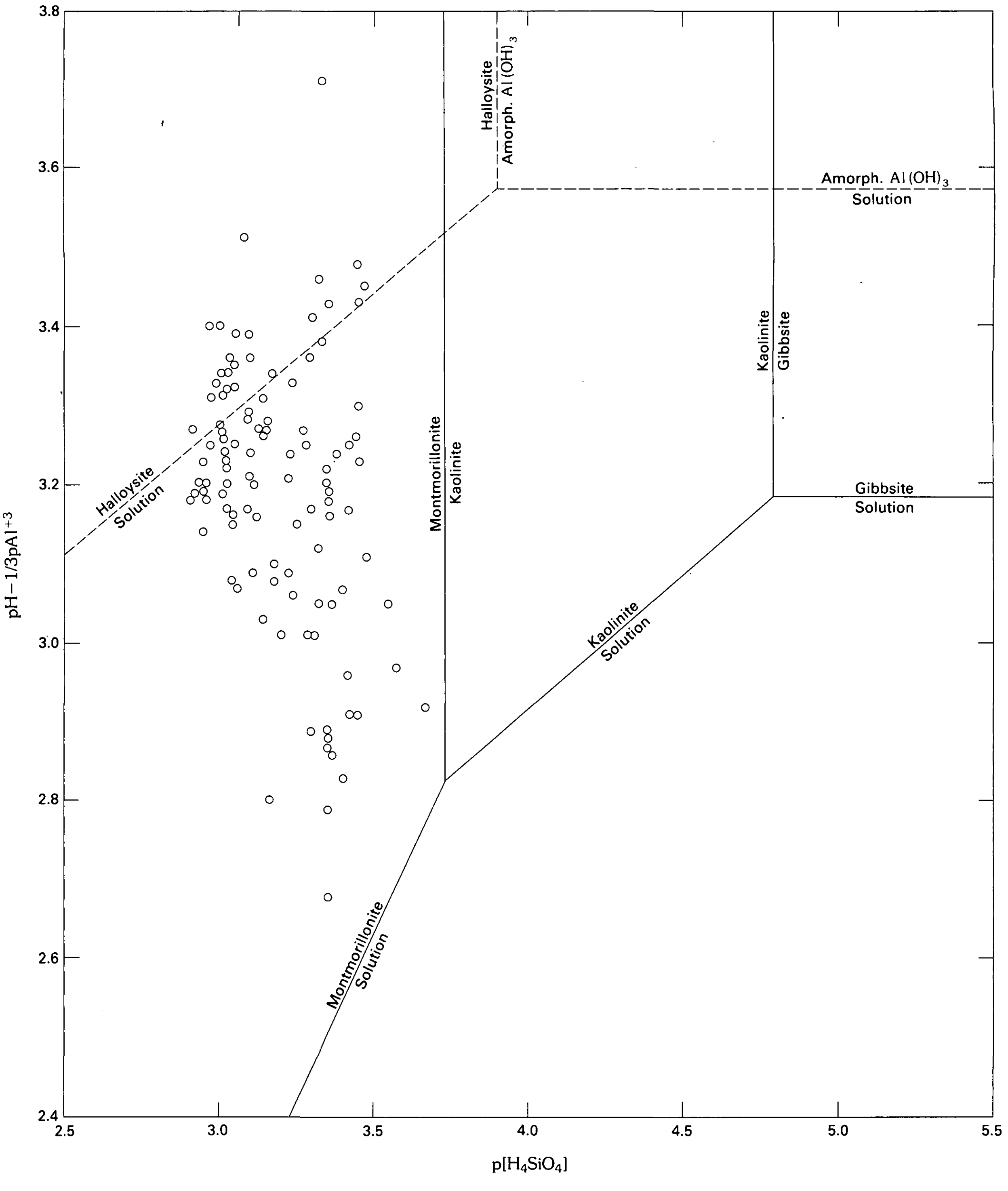

FIGURE 12.—Phase relations among minerals and aqueous solution in terms of pH-⅓pAl^{+3} and p[H_4SiO_4] at 20°C. (NOTE.—The aqueous solution is assumed to have the following ion activity ratios: log [Fe^{+3}]/[H^{+1}]^3 =4.885, log [K^{+1}]/[H^{+1}]=2.75, and log [Mg^{+2}]/[H^{+1}]^2=11.25.)

hydrogen squared and potassium to hydrogen. Aluminum is assumed to be strictly conserved in solid phases during phase transformations. Assumptions about iron and silica activities are as described at the beginning of this section on activity diagrams.

Figure 13 is actually two diagrams superimposed, so that illite, a metastable phase, can be shown. Illite is unstable with respect to montmorillonite or adularia if the three phases are considered simultaneously. The solid lines represent phase relations among the minerals

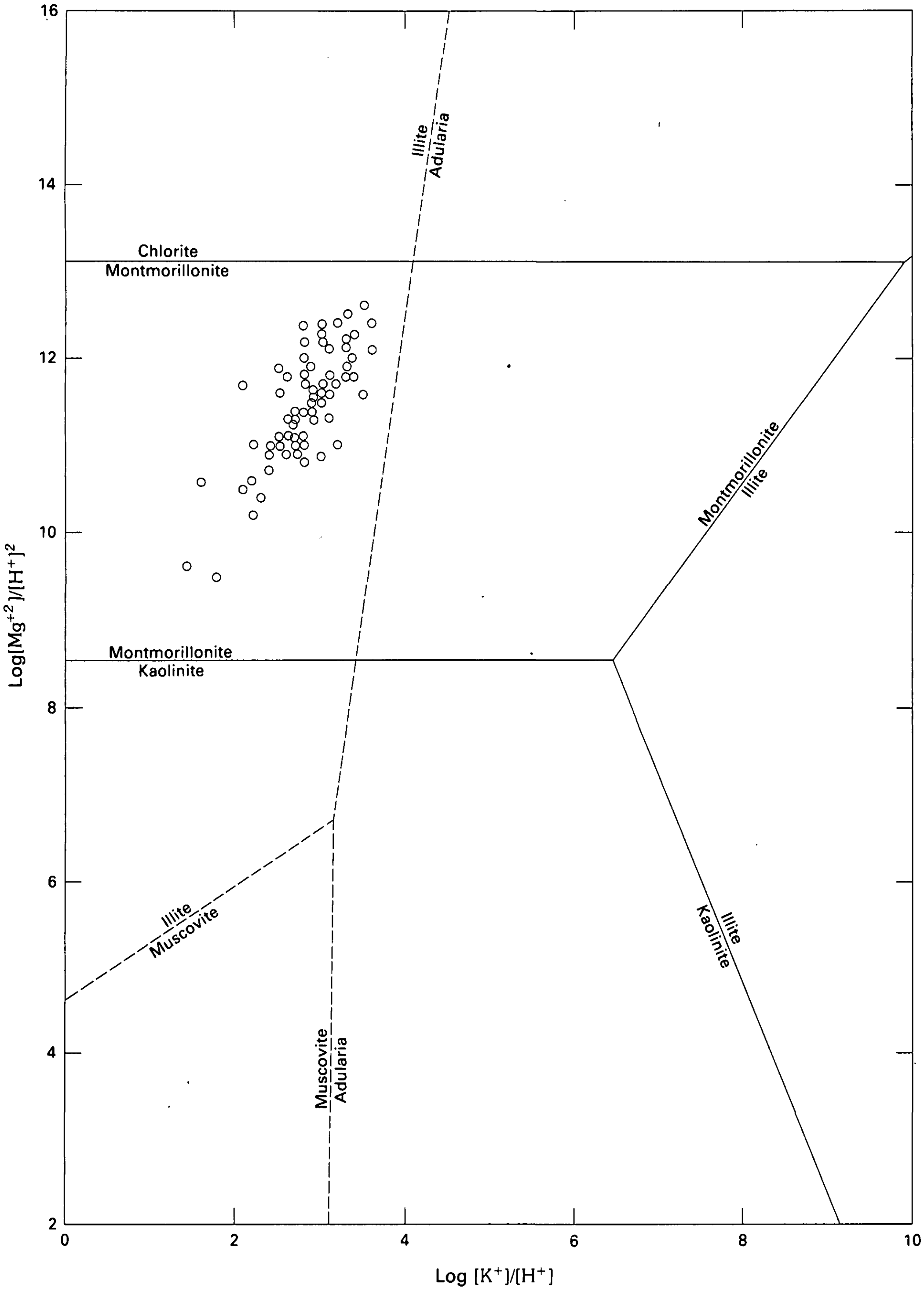

FIGURE 13.—Phase relations among minerals and coexisting aqueous solution in terms of log $[Mg^{+2}]/[H^{+1}]^2$ and log $[K^{+1}]/[H^{+1}]$ at 20°C. (NOTE.—Phase relations among chlorite, montmorillonite, illite, and kaolinite are shown by solid lines, and among illite, adularia, and muscovite by dashed lines. The aqueous solution is assumed to have the following activities of dissolved species: log $[Fe^{+3}]/[H^{+1}]^3=4.885$, log $[H_4SiO_4]=-3.21$.)

chlorite, montmorillonite, illite, and kaolinite. Among these minerals, montmorillonite is the most stable phase in equilibrium with ground water in the valley. The dashed lines represent phase relations among adularia, muscovite, and illite. Of these three minerals, illite is the most stable in contact with Sacramento Valley ground waters.

Illite is highly resistant to weathering (Berner, 1971), and most of the illite found in samples from well 19N/01W-32G is probably detrital. Some of the illite may have formed from the weathering of primary minerals. Illite has been reported to form from orthoclase (Stumm and Morgan, 1970) and from muscovite (Berner, 1971).

Log activities from ground water in the Sacramento Valley plot in the stability field of a montmorillonite having the formula and stability of Aberdeen montmorillonite. Differences in activity ratios of ions in solution will probably produce montmorillonites of somewhat different composition in the Sacramento Valley, but some form of montmorillonite will be the most stable phase. Metastable phases either form as intermediate steps during the diagenesis of primary minerals (halloysite) or persist due to resistance to weathering (illite).

SUMMARY AND CONCLUSIONS

Shallow sediments in the Sacramento Valley were laid down as alluvial deposits in a freshwater environment. These sediments, from which ground-water samples were collected, have always been in contact with freshwater. Sediments along the valley margins are coarse grained, poorly sorted, and oxidized. In the central part of the valley, flood-basin deposits are finer grained and reduced. Most of the streams entering the valley are losing streams, at least over part of their courses, and much of the ground-water recharge is from this source.

The chemistry of ground water in the valley is greatly influenced by the chemistry of this recharge from the valley margins. Approximately one-third of the variation in ground-water chemistry can be attributed to this effect. The reducing conditions and finer grained sediments in the midvalley flood basins also influence ground-water chemistry. These processes have distinct spatial patterns that produce spatial variations in the chemical character of ground water in different areas.

Six areas, or hydrochemical facies, were delineated on the basis of geology, hydrology, and distinctions in chemical composition of ground water. Two of the facies lie along the eastern margin and receive recharge from the Cascade Range and Sierra Nevada. These waters are low in dissolved solids and high in silica. Two facies are located in the midvalley flood basins, and reducing conditions there produce higher concentrations of iron, manganese, and arsenic in the ground water. While the relative concentrations of these species are higher in the flood basins than in the rest of the valley, the absolute concentrations remain fairly low. Upwelling of saline water from underlying marine sediments contributes to high dissolved-solids concentrations in ground water in the southern parts of the flood basins.

Water along the west side of the valley is low in silica, and the water grades from moderate dissolved-solids levels in the north to high dissolved-solids levels in the south. Ground water in the southwest of the valley is also high in boron. The source of the high boron and dissolved-solids concentrations is thermal springs in the Coast Ranges. Two facies were delineated along the western margin to separate the waters having moderate and high dissolved solids. Because of the heterogeneity of ground-water chemistry in the valley, division into areas having more uniform chemical compositions provides additional detail in any investigation of water chemistry.

Dissolved-solids and nitrate concentrations were examined for linear trends with time for each of the hydrochemical facies. Significant increases in both were observed in parts of the valley. On the east side of the valley, the Tuscan volcanic rocks facies showed a significant increase in dissolved solids of 0.95 (mg/L)/yr but no significant change in nitrate concentrations. The Victor Plain facies showed significant increases in both dissolved solids [1.6 (mg/L)/yr] and nitrate-nitrogen [0.036 (mg/L)/yr]. Neither Butte Basin nor Sutter Basin hydrochemical facies, in the midvalley flood basins, showed a significant trend in nitrate with time. There were very few wells with multiple nitrate measurements, however, and the lack of significant changes may be due to the small sample size. Dissolved-solids concentrations in Butte Basin have been increasing at an average rate of 1.37 (mg/L)/yr, but are unchanged in Sutter Basin.

Both the north and south alluvial fans facies, adjacent to the Coast Ranges, show significant upward trends in dissolved solids and nitrate. The south alluvial fans facies has the greatest rate of increase for dissolved solids [4.75 (mg/L)/yr] of all the facies, and the north alluvial fans facies has the greatest rate of increase for nitrate-nitrogen [0.099 (mg/L)/yr]. The midvalley basins have fine-grained poorly permeable soils that protect the ground water from contamination. Infiltration rates are slow, and reducing conditions permit the removal of nitrate by denitrification reactions. Along the valley margins, however, significant increases in dissolved solids and nitrates have occurred since the mid-1950's.

Alkali feldspars and halloysite appear to be the most significant aluminosilicate minerals affecting water chemistry. Where waters are undersaturated, dissolution of feldspars takes place, bringing the water to near saturation with respect to adularia and albite. There is a general parallel increase in aluminum and silica reflecting the solution of aluminosilicates by ground water. In Sutter Basin, the relation between log $[Al^{+3}]/[H^{+1}]^3$ and log $[H_4SiO_4]$ indicates an increase in both aluminum and silica at a ratio 1 to 3. In the Tuscan volcanic rocks facies, the relation between log $[Al^{+3}]/[H^{+1}]^3$ and log $[H_4SiO_4]$ is inverse. Rearranging the regression equation yields the same equation as for equilibrium between halloysite and an aqueous solution. The regression constant is very close to the equilibrium constant for halloysite, which supports the theory of solubility control by halloysite. Illite and halloysite were identified in sediments from the Sacramento Valley. Neither of these clay minerals is stable in the ground-water environment. The most stable clay minerals in equilibrium ground water of the valley is montmorillonite. Halloysite occurs as a mestastable intermediate step in the weathering of primary minerals to stable secondary minerals.

REFERENCES

Back, William, 1966, Hydrochemical facies and ground-water flow patterns in northern part of Atlantic Coastal Plain: U.S. Geological Survey Professional Paper 498-A, 42 p.

Barnes, Ivan, O'Neil, J. R., Rapp, J. B., and White, D. E., 1973, Silica-carbonate alteration of serpentine: Wall rock alteration in mercury deposits of the California Coast Ranges: Economic Geology, v. 68, no. 3, p. 388–398.

Barnes, R. B., 1975, The determination of specific forms of aluminum in natural water: Chemical Geology, v. 15, no. 3, p. 177–191.

Bennett, G. D., 1979, Regional ground water systems analysis: Water Spectrum, Fall 1979, p. 36–42.

Berner, R. A., 1971, Principles of chemical sedimentology: New York, McGraw-Hill, 240 p.

Berner, R. A., and Holdren, Jr., G. R., 1979, Mechanisms of feldspar weathering, II. Observations of feldspars from soils: Geochimica et Cosmochimica Acta, v. 43, no. 8, p. 1173–1186.

Bertoldi, G. L., 1976, Chemical quality of ground water in the Tehama-Colusa Canal service area, Sacramento Valley, California: Menlo Park, Calif., U.S. Geological Survey Water-Resources Investigations 76–92, 44 p.

———1979, A plan to study the aquifer system of the Central Valley of California: U.S. Geological Survey Open-File Report 79–1480, 48 p.

Bryan, Kirk, 1923, Geology and ground-water resources of Sacramento Valley, California: U.S. Geological Survey Water-Supply Paper 495, 285 p.

Busenberg, Eurybiades, 1978, The products of the interaction of feldspars with aqueous solutions at 25°C: Geochimica et Cosmochimica Acta, v. 42, no. 11, p. 1679–1686.

California Department of Water Resources, 1978a, Evaluation of ground water resources: Sacramento Valley: California Department of Water Resources Bulletin 118–6, 136 p.

———1978b, The Sacramento Valley water use survey, 1977: California Department of Water Resources Bulletin 168, 98 p.

California Division of Mines and Geology, 1966, Geology of northern California: California Division of Mines and Geology Bulletin 190, 508 p.

Curtin, George, 1971, Hydrogeology of the Sutter Basin, Sacramento Valley, California: Unpublished M. S. Thesis, The University of Arizona, 83 p.

Darken, L. S., and Gurry, R. W., 1953, Physical chemistry of metals: New York, McGraw-Hill, 535 p.

Davis, J.C., 1973, Statistics and data analysis in geology: New York, John Wiley and Sons, 550 p.

Drake, J. J., and Harmon, R. S., 1973, Hydrochemical environments of carbonate terrains: Water Resources Research, v. 9, no. 4, p. 949–957.

El-Ashry, M. T., 1980, Ground-water salinity problems related to irrigation in the Colorado River Basin: Ground Water, v. 18, no. 1, p. 37–45.

Feth, J. H., Roberson, C. E., and Polzer, W. L., 1964, Sources of mineral constituents in water from granitic rocks, Sierra Nevada, California and Nevada: U.S. Geological Survey Water-Supply Paper 1535–I, 70 p.

Fogelman, R. P., 1975, Descriptions and chemical analyses for selected wells in the Tehama-Colusa Canal service area, Sacramento Valley, California: U.S. Geological Survey Open-File Report, 52 p.

———1976, Descriptions and chemical analyses for selected wells in the central Sacramento Valley, California: U.S. Geological Survey Open-File Report 76–472, 71 p.

———1983, Ground-water quality in the Sacramento Valley, California—Water types and potential nitrate and boron problem areas: U.S. Geological Survey Hydrologic Investigations Atlas, HA–651.

Fogelman, R. P., and Rockwell, G. L., 1977, Descriptions and chemical analyses for selected wells in the eastern Sacramento Valley, California: U.S. Geological Survey Open-File Report 77–486, 82 p.

Garrels, R. M., and Christ, C. L., 1965, Solutions, minerals, and equilibria: San Francisco, Calif., Freeman, Cooper, and Co., 450 p.

Helgeson, H. C., Brown, T. H., and Leeper, R. H., 1969, Handbook of theoretical activity diagrams depicting chemical equilibria in geologic systems involving an aqueous phase at one atm. and 0° to 300°C: San Francisco, Calif., Freeman, Cooper, and Co., 450 p.

Holdren, Jr., G. R., and Berner, R. A., 1979, Mechanisms of feldspar weathering, I. Experimental studies: Geochimica et Cosmochimica Acta, v. 43, no. 8, p. 1161–1171.

Kennedy, V. C., Zellweger, G. W., and Jones, B. F., 1974, Filter pore-size effects on the analyses of Al, Fe, Mn, and Ti in water: Water Resources Research, v. 10, no. 4, p. 785–790.

Kern County Water Agency, 1979, Ground water quality model project, San Joaquin Valley Basin, Kern County, California: Agricultural Water Quality Management Group, Bakersfield, Calif., 60 p.

Kittrick, J. A., 1969, Soil minerals in the Al_2O_3-SiO_2-H_2O system and a theory of their formation: Clays and Clay Minerals, v. 17, no. 3, p. 157–167.

———1971, Stability of montmorillonites: II. Aberdeen montmorillonite: Soil Science Society of America Proceedings, v. 35, no. 5, p. 820–823.

Klein, J. M., and Bradford, W. L., 1979, Distribution of nitrate and related nitrogen species in the unsaturated zone, Redlands and vicinity, San Bernardino County, California: Menlo Park, Calif., U.S. Geological Survey Water-Resources Investigations 79–60, 81 p.

Marchand, D. E., and Allwardt, Alan, 1981, Late Cenozoic stratigraphic units, northeastern San Joaquin Valley, California: U.S. Geological Survey Bulletin 1470, 70 p.

Matalas, N. C., Slack, J. R., and Wallis, J. R., 1975, Regional skew in search of a parent: IBM Thomas J. Watson Research Center, Yorktown Heights, N.Y., 243 p.

Olmsted, F. H., and Davis, G. H., 1961, Geologic features and ground-water storage capacity of the Sacramento Valley, California: U.S. Geological Survey Water-Supply Paper 1497, 241 p.

Paces, T., 1973, Steady-state kinetics and equilibrium between ground water and granitic rock: Geochimica et Cosmochimica Acta, v. 37, no. 12, p. 2641–2663.

———1978, Reversible control of aqueous aluminum and silica during the irreversible evolution of natural waters: Geochimica et Cosmochimica Acta, v. 42, no. 10, p. 1487–1493.

Plummer, L. N., Jones, B. F., and Truesdell, A. H., 1978, WATEQF—A Fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters: U.S. Geological Survey Water-Resources Investigations 76–13, 63 p.

Rummel, R. J., 1970, Applied factor analysis: Northwestern University Press, Evanston, Illinois, 617 p.

Shlemon, R. J., 1967, Quaternary geology of northern Sacramento County, California: Sacramento Geological Society Guidebook Annual Field Trip, 60 p.

Stumm, Werner, and Morgan, J. J., 1970, Aquatic chemistry: New York, Wiley-Interscience, 583 p.

Tardy, Y., 1971, Characterization of the principal weathering types by the geochemistry of waters from some European and African crystalline massifs: Chemical Geology, v. 7, no. 4, p. 253–271.

Truesdell, A. H., and Jones, B. F., 1974, WATEQ, a computer program for calculating chemical equilibria of natural waters: U.S. Geological Survey Journal of Research, v. 2, no. 2, p. 233–248.

Waring, G. A., 1965, Thermal springs of the United States and other countries of the world—A summary: U.S. Geological Survey Professional Paper 492, 383 p.

White, A. F., 1979, Geochemistry of ground water associated with tuffaceous rocks, Oasis Valley, Nevada: U.S. Geological Survey Professional Paper 712–E, 25 p.

White, D. E., Barnes, Ivan, and O'Neill, J. R., 1973, Thermal and mineral waters of nonmeteoric origin, California Coast Ranges: Geological Society of America Bulletin, v. 84, no. 2, p. 547–560.

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