Geochemistry of Ground Water Associated with Tuffaceous Rocks, Oasis Valley, Nevada

By A. F. WHITE

HYDROLOGY OF NUCLEAR TEST SITES

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SYSTEM OF MEASUREMENT UNITS

The following report uses both the metric and the U.S. customary systems of units. In the text the metric units are given first, and the equivalent measurement in U.S. customary units is given in parentheses. The units are frequently abbreviated, using the notations shown below. The metric units can be converted to U.S. customary units by multiplying by the factors given in the following list.

Metric unit *To convert*	*Multiply by*	*U.S customary unit* *To obtain*
Kilometer (km)	0.622	Mile (mi).
Meter (m)	3.281	Foot (ft).
Square kilometer (km^2)	.387	Square mile (mi^2).
Meter per kilometer (m/km)	5.280	Foot per mile (ft/mi).
Cubic hectometer (hm^3)	811.030	Acre-feet (acre-ft)
Liter per second (L/s)	15.850	Gallon per minute (gal/min)

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GEOCHEMISTRY OF GROUND WATER ASSOCIATED WITH TUFFACEOUS ROCKS, OASIS VALLEY, NEVADA

By A. F. WHITE

ABSTRACT

Oasis Valley is an arid intermontane basin located in southern Nevada. The two principal aquifers are rhyolitic tuffs of Tertiary age in the highlands, and tuff-derived alluvium of Pleistocene and Holocene age in the valley bottom. Regional similarities and trends in the aqueous chemistry indicate that most of the recharge entering the Oasis Valley ground-water system probably is the result of ground-water inflow from Pahute Mesa, Gold Flat, and other areas to the north and east. Mass-balance calculations show that about half the water recharged to Oasis Valley discharges through evapotranspiration, and the rest exits by flow through the alluvium southward toward the Amargosa Desert.

Most of the water in the basin has moved from areas of recharge in the highlands through the fracture system in the tuffaceous rocks to the alluvial material in the valley floor. The solute concentrations of sodium and silica suggest that hydrolysis and incongruent dissolution of volcanic glass are the principal reactions in the tuffaceous aquifer. Chloride is also leached preferentially relative to fluoride. Stability calculations, based on recently reported solubility data for montmorillonite of a chemical composition similar to that found in the tuffs in areas adjacent to Oasis Valley, show that montmorillonite is a stable weathering product formed by the ground water. The water is thermodynamically saturated with respect to silica gel but undersaturated in terms of analcime, a mineral which occurs extensively in zeolitized zones within the tuffs. This lack of saturation suggests that zeolitization occurs in localized geochemical environments, which are not generally reflected in the ground-water composition found in Oasis Valley.

Ground water infiltrates the alluvial aquifer from the tuffs via springs and subsurface flow. The close proximity of the water table in the alluvium to the ground surface promotes evapotranspiration, and evapotranspiration causes a decrease in the volume of ground water and an increase in chemical concentration. Colinear increases in concentrations of selected solute species demonstrate that water contained in both the tuffaceous aquifer and the alluvium has the same generic origin. Such linearity also suggests that sodium and chloride are neither selectively added nor removed from the aqueous system, and that bicarbonate is only locally affected by dissolution and precipitation of calcite. Calcium concentrations are controlled by dissolution of calcium sulfate minerals present in lacustrine deposits or as oxidation products of hydrothermal alteration and by precipitation of calcite. Fluoride reaches a limiting concentration controlled by fluorite saturation. Aqueous potassium concentrations are probably controlled by adsorption and fixation by degraded clays common to arid soil zones and also by uptake by the vegetative cover.

INTRODUCTION

The study of the geology, geochemistry, and hydrology of Oasis Valley, Nye County, Nevada, was begun in 1967 as part of a program to determine the source and eventual destination of ground water under and surrounding the Nevada Test Site. This program was undertaken by the U.S. Geological Survey in cooperation with the U.S. Department of Energy (formerly the U.S. Energy Research and Development Administration). The geochemical characteristics discussed in this paper are meant to lend insight into the probable history of the ground water of Oasis Valley and to contribute to the general understanding of geochemical processes that govern the composition of ground water associated with tuffaceous aquifers.

PREVIOUS WORK

The geochemical nature of the ground water of Oasis Valley was described briefly by Malmberg and Eakin (1962); their description is based on samples collected from several wells and springs within the area. They classified the water as being a sodium bicarbonate type commonly found in areas of Nevada underlain by tuffaceous deposits of Tertiary age. Malmberg and Eakin (1964) later elaborated upon the geochemistry of fluoride, high concentrations of which are found in the domestic water supply of Beatty (fig. 1).

The economic geology of the Bullfrog Hills, parts of which are within the western part of the Oasis Valley drainage (fig. 1), has been described by Ransome, Emmons, and Garrey (1910). The geology and structural history of the Bullfrog Hills was enlarged upon by Cornwall and Kleinhampl (1964). Geologic quadrangle maps of parts of Oasis Valley, including Bare Mountain (Cornwall and Kleinhampl, 1961), Thirsty Canyon (O'Connor, Anderson, and Lipman, 1966), and Timber Mountain (Carr and Quinlivan, 1966), have been published.

ACKNOWLEDGMENTS

The author especially wishes to acknowledge the help of W. A. Beetem and R. A. Young who initiated the study of Oasis Valley and who carried out the sampling program. The author wishes to express thanks to B. F. Jones and H. C. Claassen for valuable comments and

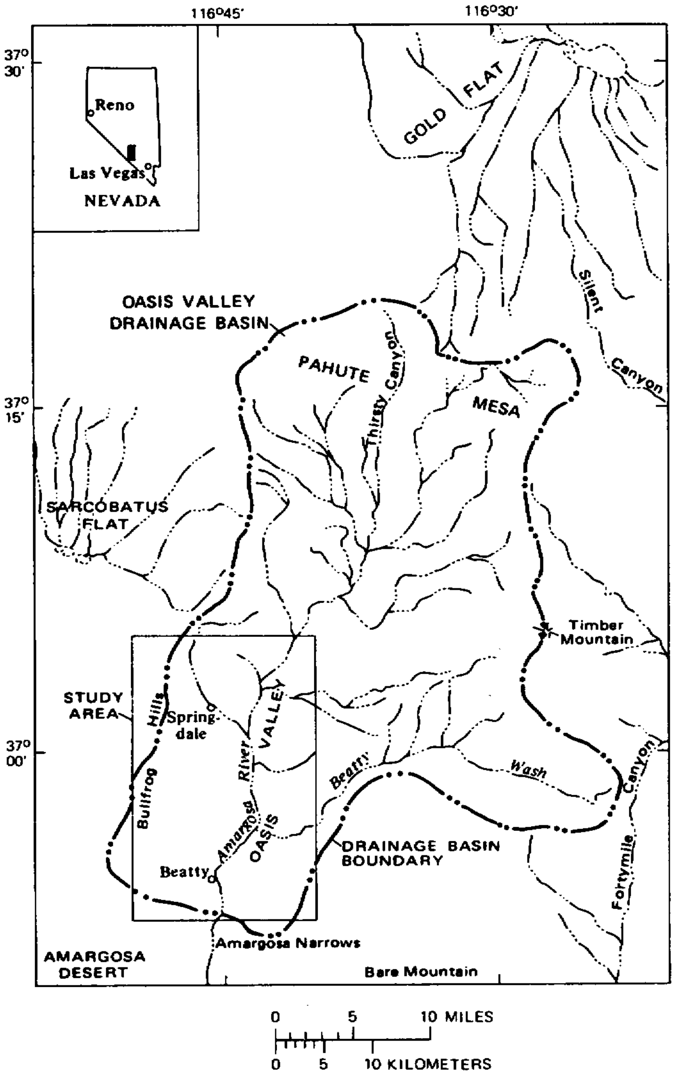


FIGURE 1.—Location of Oasis Valley drainage basin and study area.

criticisms on the concepts presented in this paper and to P. P. Orkild for the use of unpublished geologic maps of the area. Appreciation is also expressed to the U.S. Department of Energy for support given to the project.

METHODS OF INVESTIGATION

Water samples were collected from 29 springs and wells in the Oasis Valley area. The locations of the sampling sites are shown in figure 2. Descriptions of the individual sites are given in table 1. Specific conductance, temperature, pH, and alkalinity were determined in the field. These parameters plus additional analyses performed in the laboratories of the U.S. Geological Survey are presented in tables 2 and 3.

The computer program, WATEQ (Truesdell and Jones, 1974), was used to calculate equilibrium relationships between solute species and various mineral phases. Unless otherwise noted, thermodynamic values cited in this paper are those listed in WATEQ. Theoretical activity diagrams (Helgeson and others, 1969) were also employed to facilitate prediction and interpretation of chemical equilibrium. The reader is referred to Garrels and Christ (1965) and Hem (1970) for a more complete discussion of geochemical concepts presented in this paper, including the use of ionactivity products, solubility products, mineral stability fields, and the significance of thermodynamic undersaturation and supersaturation.

WELL-NUMBERING SYSTEM

Numbers assigned to wells and springs in Nevada are based on the land net established by the General Land Office and its successor, the U.S. Bureau of Land Management. The locations are referred to the Mount Diablo baseline and meridian. Thus the well number 10S/47-27aaal refers to a well in Township 10 South as indicated by the number and letter before the slash. The number after the slash, 47, is the Range east of the Mount Diablo meridian. Because all ranges in Nevada are east of that meridian, the letter E is disregarded. The number after the dash, 27, is the number of the section, and the letters refer to the quarter, quarter-quarter, and the quarter-quarter-quarter section in which the well was found. The quarter sections are labeled a, b, c, and d counter-clockwise in the section.

GEOGRAPHIC AND GEOLOGIC SETTING

Oasis Valley (fig. 1) is defined topographically as the central part of an arid intermontane basin which contains the headwaters of the Amargosa River. Thirsty Canyon and Springdale tributaries (fig. 2) enter Oasis Valley from the north, Beatty Wash and Fluorspar Canyon from the east, and ephemeral stream drainage of the Bullfrog Hills from the west. The Amargosa River and these tributaries are ephemeral streams that carry surface flow only during periods of heavy runoff. The entire drainage basin contains approximately 1,200 sq km (460 sq mi) of mountainous and greatly dissected terrane. Timber Mountain, with an altitude of 2,270 m (7,450 ft), is the highest point in the area, and the Amargosa Narrows, with an altitude of 975 m (3,200 ft), is the lowest point. Beatty, the principal town in the basin, is 185 km (115 mi) northwest of Las Vegas.

ROCKS OF PALEOZOIC AGE

The oldest rocks exposed in the Oasis Valley drainage basin are of Paleozoic age. They are exposed principally in the mountains in the extreme southern parts

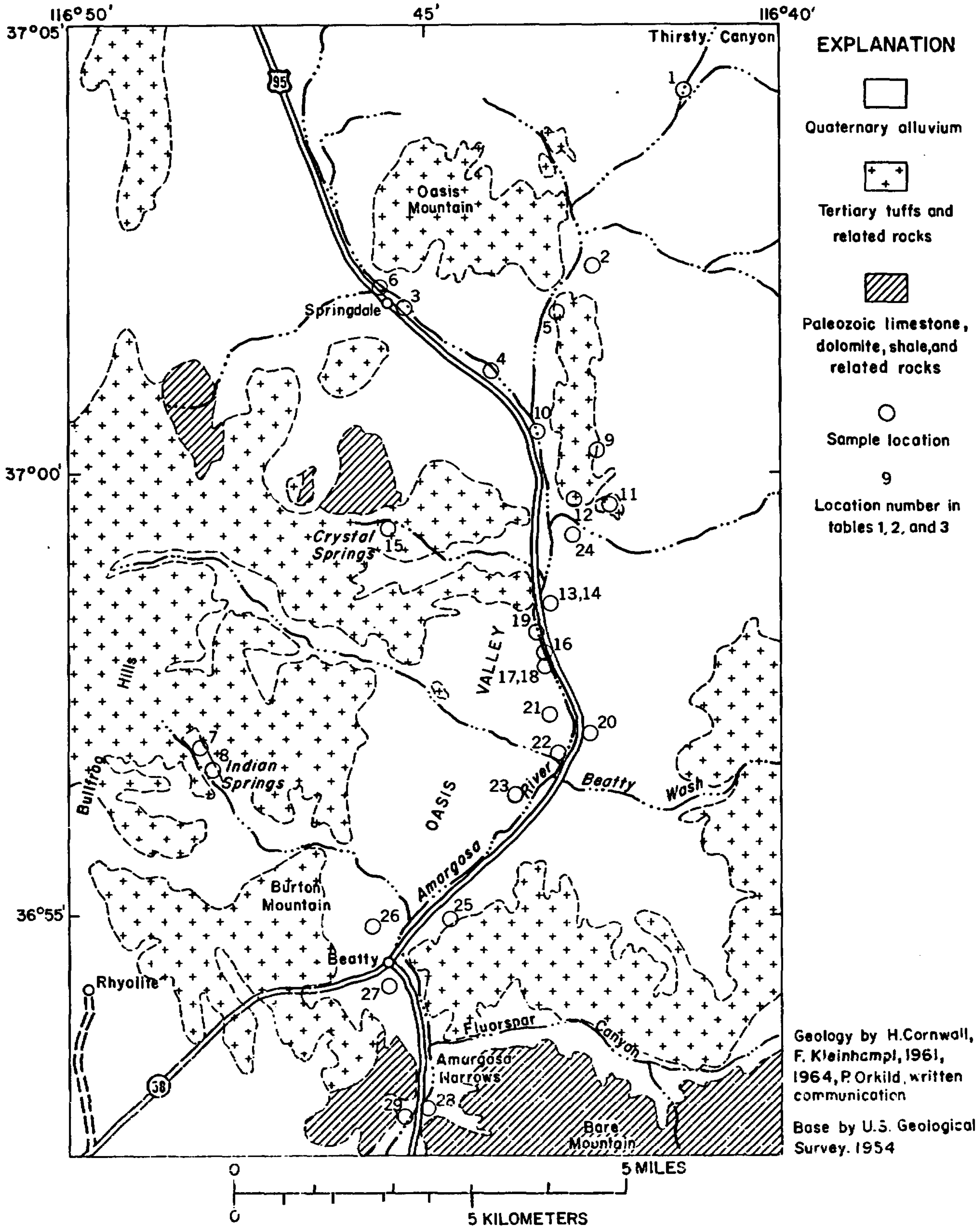


FIGURE 2.—Geology and sampling sites.

TABLE 1.—*Description of sampling sites*

[Qal, alluvium of Quaternary age; Tv, volcanic rock of Tertiary age; samples collected July 3–6, 1967]

Sample site number	Site coordinates	Site name	Sample source	Probable aquifer type	Depth		Discharge	
					m	ft	L/s	gal/min
1	10S/47-14bab	--	Spring	Qal	--	--	6	100
2	10S/47-27cba	--	Well	Qal	2	6	--	--
3	10S/47-31aab	--	Spring	Qal	--	--	.7	11
4	10S/47-32dda	--	do	Qal	--	--	14	225
5	10S/47-33aab	--	do	Qal	--	--	16	255
6	10S/47-30dcc		Well	Qal	37	121	3	50
7	11S/46-26bbb	Upper Indian Spring	Spring	Tv	--	--	--	--
8	11S/46-26bcc	Lower Indian Spring	do	Tv	--	--	.5	8
9	11S/47-3cdb	--	do	Tv	--	--	2.5	40
10	11S/47-4cad	--	do	Qal	--	--	.6	10
11	11S/47-10caa	--	do	Tv	--	--	3.1	49
12	11S/47-10bcc	--	do	Tv	--	--	--	--
13	11S/47-16dcd	Burro Hot Springs	do	Tv	--	--	--	--
14	11S/47-16bdc	do	do	Tv	--	--	--	--
15	11S/47-18acd	Crystal Springs	do	Tv	--	--	--	--
16	11S/47-21acc	--	do	Qal	--	--	--	--
17	11S/47-21dbb	--	Well	Qal	--	--	1.6	26
18	11S/47-21aba	--	Spring	Qal	--	--	--	--
19	11S/47-21aba	--	do	Tv	--	--	--	--
20	11S/47-27cba	--	Well	Tv	17	55	1	20
21	11S/47-28aac	--	do	Qal	8	25	.06	1
22	11S/47-28dac	Ute Spring	Spring	Qal	--	--	1.6	25
23	11S/47-33bac	--	do	Tv	--	--	1.6	25
24	11S/47-10ccb	--	do	Tv	--	--	--	--
25	12S/47-5cda	Beatty Spring	do	Tv	--	--	--	--
26	12S/47-6cdd	--	Well	Qal	55	180	5	80
27	12S/47-7dbd	--	do	Qal	91	300	14	230
28	12S/47-20bbb	--	do	Qal	--	--	6	100
29	12S/47-19adc	--	do	Qal	--	--	--	--

TABLE 2.—*Analyses of selected major chemical constituents*

[Sampling-site numbers keyed to figures; samples collected July 3–6, 1967. Qal = Alluvium of Quaternary age; Tv = Volcanics of Tertiary age. Concentrations in millimoles per liter, except as indicated]

Sampling-site number	Probable aquifer source	Temperature (°C)	pH	Dissolved constituents									Total dissolved solids (mg/L)
				calcium (Ca)	magnesium (Mg)	sodium (Na)	potassium (K)	bicarbonate (HCO_3)	chloride (Cl)	fluoride (F)	sulfate (SO_4)	silica (SiO_2)	
1	Qal	29.0	8.1	0.18	0.01	6.22	0.21	3.39	1.44	0.22	0.86	0.95	458
2	Qal	19.0	7.7	.55	.06	7.44	.22	4.57	1.83	.99	1.06	1.03	573
3	Qal	19.5	7.6	.58	.18	4.35	.20	3.75	1.18	.13	.55	1.18	421
4	Qal	22.0	7.6	.75	.22	5.96	.00	5.08	1.04	.12	1.00	1.03	523
5	Qal	22.0	7.8	.75	.19	7.35	.23	4.85	1.92	.23	1.07	.90	584
6	Qal	22.5	7.8	.60	.19	4.35	.20	3.90	1.13	.09	.61	1.20	424
7	Tv	26.5	8.7	.00	.01	2.57	.04	1.90	.39	.02	.15	.73	192
8	Tv	21.0	7.9	.15	.04	2.48	.04	2.07	.42	.02	.18	.80	213
9	Tv	23.0	8.2	.40	.04	5.31	.12	3.00	1.27	.15	.98	.78	420
10	Qal	21.0	7.7	.65	.18	9.70	.22	6.25	2.26	.27	1.35	1.03	726
11	Tv	24.0	8.1	.35	.03	8.53	.06	5.41	1.52	.32	1.13	.63	583
12	Tv	18.5	7.6	.35	.02	6.79	.18	4.79	1.18	.24	.95	.65	511
13	Tv	36.5	7.8	.45	.02	7.53	.20	4.39	1.33	.32	1.32	1.00	572
14	Tv	36.5	7.8	.42	.02	7.13	.13	4.15	1.21	.30	1.25	1.07	546
15	Tv	24.0	7.7	.55	.13	2.18	.09	2.33	.59	.03	.23	.75	25[illegible]
16	Qal	31.5	7.7	.58	.12	10.09	.22	6.10	1.95	.32	1.65	1.00	750
17	Qal	29.0	7.7	.62	.13	10.57	21	6.44	2.03	.32	1.74	.93	783
18	Qal	26.0	7.9	.65	.15	10.70	.21	6.46	2.03	.32	1.74	.90	777
19	Tv	41.0	7.6	.32	.02	6.53	.20	3.65	.99	.32	1.21	90	509
20	Tv	21.5	8.0	.90	.21	5.00	.28	3.63	2.62	.37	2.27	.96	396
21	Qal	18.0	9.1	.25	.19	13.70	.23	8.39	1.92	.34	1.76	75	997
22	Qal	21.0	8.2	.21	.00	10.83	.06	5.03	.76	.20	.73	.77	737
23	Tv	34.0	8.3	.30	.03	4.87	.12	2.84	1.27	.14	.85	.83	355
24	Tv	21.0	8.2	.32	.11	5.39	.15	3.03	.73	.20	.73	1.00	414
25	Tv	24.0	7.9	.80	.18	4.61	.19	3.21	1.07	.02	97	.90	384
26	Qal	21.6	7.9	.68	.13	4.57	.26	3.47	2.06	.32	1.86	--	440
27	Qal	20.0	7.7	.63	.15	11.14	.26	6.49	2.06	.32	1.36	1.10	814
28	Qal	18.5	7.8	.68	.15	11.05	.26	6.39	2.17	.31	1.91	1.12	820
29	Qal	20.0	7.7	.95	.23	12.62	.26	7.20	2.82	.33	2.60	1.12	1,040

TABLE 3.—*Analyses of selected minor chemical constituents*

[Sampling-site numbers keyed to figures; samples collected July 3–6, 1967. Concentrations in micromoles per liter]

Sampling-site number	Dissolved constituents					
	Boron (B)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Strontium (Sr)	Barium (Ba)
1	--	0.03	0.36	0.22	0.17	0.03
2	21.3	.01	.18	.26	1.71	.09
3	45.3	.13	.20	.15	2.05	.09
4	53.6	.03	.18	.074	4.45	.17
5	31.4	.05	.32	.45	2.17	.18
6	47.1	.02	.32	.37	2.17	.09
7	15.7	.02	.07	.41	.10	.01
8	16.6	.02	.16	.55	.34	.02
9	17.6	.02	.36	.45	1.08	.06
10	41.6	.02	.14	.26	3.19	.14
11	19.4	.05	.27	.11	1.48	.04
12	--	.03	.81	1.48	.46	.04
13	18.5	.09	.43	.26	1.37	.17
14	17.6	.05	1.52	.03	1.37	.19
15	10.2	.03	.25	.15	.51	.02
16	36.0	.03	.89	3.34	2.51	.03
17	35.1	.08	1.07	.19	2.86	.03
18	30.5	.03	.53	.26	2.97	.03
19	15.7	.05	.18	.04	1.37	.20
20	14.8	.05	1.07	1.11	.23	.02
21	38.8	.03	1.25	.26	4.56	.11
22	34.2	.05	8.41	.93	1.03	.02
23	--	.06	.20	.30	.23	.01
24	16.6	.02	.16	.52	.68	.04
25	20.3	.05	.18	.26	.86	.02
26	43.4	.03	1.07	.11	1.37	.04
27	46.2	.03	.89	1.12	1.37	.06
28	53.6	.06	.16	1.67	.11	.07
[1]29	--	--	--	--	--	--

[1] No analyses for sample site 29.

of Oasis Valley (fig. 2) and to a lesser extent in the Bullfrog Hills southwest of Springdale. These rocks have been subjected to intense thrust faulting and folding. The formations range in age from Early Cambrian to Late Mississippian and have a composite thickness of about 7,600 m (25,000 ft). The sequence in Oasis Valley consists of stratified layers of shale, siltstone, quartzite, limestone, and dolomite. Carbonate rocks predominate in the upper half of the sequence, whereas shales and related rocks make up most of the lower half.

ROCKS OF TERTIARY AGE

Most of the bedrock exposed in Oasis Valley consists of ash-flow tuff, ash-fall tuff, rhyolite flows, and minor basalt flows of Tertiary age that emanated from local volcanic centers. The formations of most interest in the Oasis Valley drainage basin are the Paintbrush Tuff, the Timber Mountain Tuff, and the Thirsty Canyon Tuff. The formations are multiple-flow units ranging in rock type from rhyolite to quartz latite. The rocks range gradationally from nonwelded to densely welded. Many exposures display extensive jointing and fracturing.

ALLUVIUM OF PLEISTOCENE AND HOLOCENE AGE

Much of the surface area of Oasis Valley is covered with alluvium. Cornwall and Kleinhampl (1961) and other workers have mapped this alluvial cover as two separate units. The older unit, classified as gravels of Pleistocene age, represents old dissected alluvial fans. The younger unit, presently forming alluvial fans, is mapped as alluvium of Holocene age. The gravel in these newer fans grades into sand and silt toward the topographic bottom of Oasis Valley. With the exception of alluvium associated with rocks of Paleozoic age found in the extreme southern part of Oasis Valley, both units are composed of detritus originating from the tuff formations. The exact thickness of the total alluvial cover is not known, but it is estimated by Malmberg and Eakin (1962) to be as much as several thousand feet in the central part of Oasis Valley. The alluvium is much thinner in the southern part of Oasis

Valley. Based on unpublished geophysical data of the U.S. Geological Survey, the estimated thickness of alluvium resting on the Paleozoic bedrock within the Amargosa Narrows (fig. 2) is 4–5 m (12–16 ft).

HYDROLOGY

SURFACE WATER

The Amargosa River flows in a few reaches in the central part of Oasis Valley during part of the winter and early spring until evapotranspiration becomes sufficient to draw down the potentiometric surface below the stream bottom. Flow at other times is incidental with thunderstorms in the headwaters of Thirsty Canyon or Beatty Wash. Surface flow from springs also occurs along short reaches of the valley floor.

GROUND WATER

The two principal aquifers in the Oasis Valley basin are tuffaceous rocks in the highlands and alluvium beneath the valley floor. Blankennagel and Weir (1973) concluded that the ground water in the tuffaceous rocks related to those surrounding Oasis Valley was transmitted principally through extensive fracture systems produced by contractional cooling during solidification and by post-depositional faulting. Where such rocks are saturated, are broken by recent faulting, or intersect the land surface, ground water issues as springs and seeps. Such is the case for several sample locations shown in figure 2 along the east side of Oasis Valley between Beatty Wash and Thirsty Canyon.

Ground water infiltrates from springs and subsurface flow into the valley-fill alluvium which occurs principally along the Amargosa River and its tributaries. At most places, this valley fill is saturated to within several feet of the surface. Malmberg and Eakin (1962) suggested that where the cross-sectional area of the alluvial fill is decreased by underlying, less permeable material, water is forced to the surface and issues as springs, seeps, and swampy areas. Some artesian wells have been developed in alluvium where ground water is confined beneath layers of clay.

Figure 3 shows the approximate locations of the ground-water flow paths in the alluvium; the locations are based on topographic and geographic distributions of the valley fill.

RECHARGE AND DISCHARGE

Malmberg and Eakin (1962) estimated an average annual recharge from precipitation within the Oasis Valley drainage basin of 0.31 hm^3 (250 acre-ft), and an annual discharge from Oasis Valley by evapotranspiration and ground-water underflow of 3.0 hm^3 (2,400 acre-ft). Based on the above estimates, they postulated a significant inflow of ground water from outside the Oasis Valley drainage basin, probably as recharge from Pahute Mesa, Gold Flat, and other areas to the north and northeast (fig. 1). Blankennagel and Weir (1973) substantiated this conclusion by defining a southwestward-trending potentiometric surface under Pahute Mesa in the direction of Oasis Valley. The total underflow passing southwestward through tuffaceous rocks beneath Pahute Mesa was estimated at 10 hm^3 (8,100 acre-ft) annually, only part of which probably recharges Oasis Valley. Of this total volume, perhaps 3.9 hm^3 (3,200 acre-ft) is recharge from precipitation on Pahute Mesa, and the remainder may be underflow from Gold Flat and other areas to the north. Altitudes of the water table indicate a gradient of approximately 4 m/km (20 ft/mi) between Gold Flat and the upper spring in Oasis Valley, (sample location 1 in fig. 2). Winograd and Thordarson (1975), in defining the general hydrologic systems in the south-central Great Basin, also suggested that the Oasis Valley ground-water system was recharged by underflow through tuffaceous rocks from Pahute Mesa and Gold Flat.

Evapotranspiration accounts for much of the ground water discharged from Oasis Valley. The principal species of phreatophytes, including salt grass, Bermuda grass, greasewood, and salt bush, occur along the flood plain of the Amargosa River. The average depth to water below land surface in most phreatophyte zones is 2–3 m (6–10 ft). Evaporation also occurs locally from spring pools and swampy or seep areas. Based on phreatophyte cover, open-water acreage, and assumed rates of evapotranspiration, Malmberg and Eakin (1962) estimated an evapotranspiration discharge of 2.5 hm^3 (2,000 acre-ft). They estimated the average ground-water discharge southward toward the Amargosa Desert (fig. 1) through the thin alluvium overlying the Paleozoic bedrock in the Amargosa Narrows to be 0.5 hm^3 (400 acre-ft) annually.

GEOCHEMICAL ENVIRONMENTS

The geochemical history of the Oasis Valley ground water can be broadly classified into two stages based on differing aquifer characteristics. Most ground water in Oasis Valley has presumably moved from areas of recharge through the fracture system of the tuffaceous aquifer. In this first stage, dissolved carbon dioxide originating in the soil zone of the recharge area reacts with mineral phases in the tuffaceous rocks. The specific chemical composition of the ground water at any given point along the flow path is a function of the kinetic rate of reaction, and hence the total residence time spent within the tuffaceous aquifer. Ground wa-

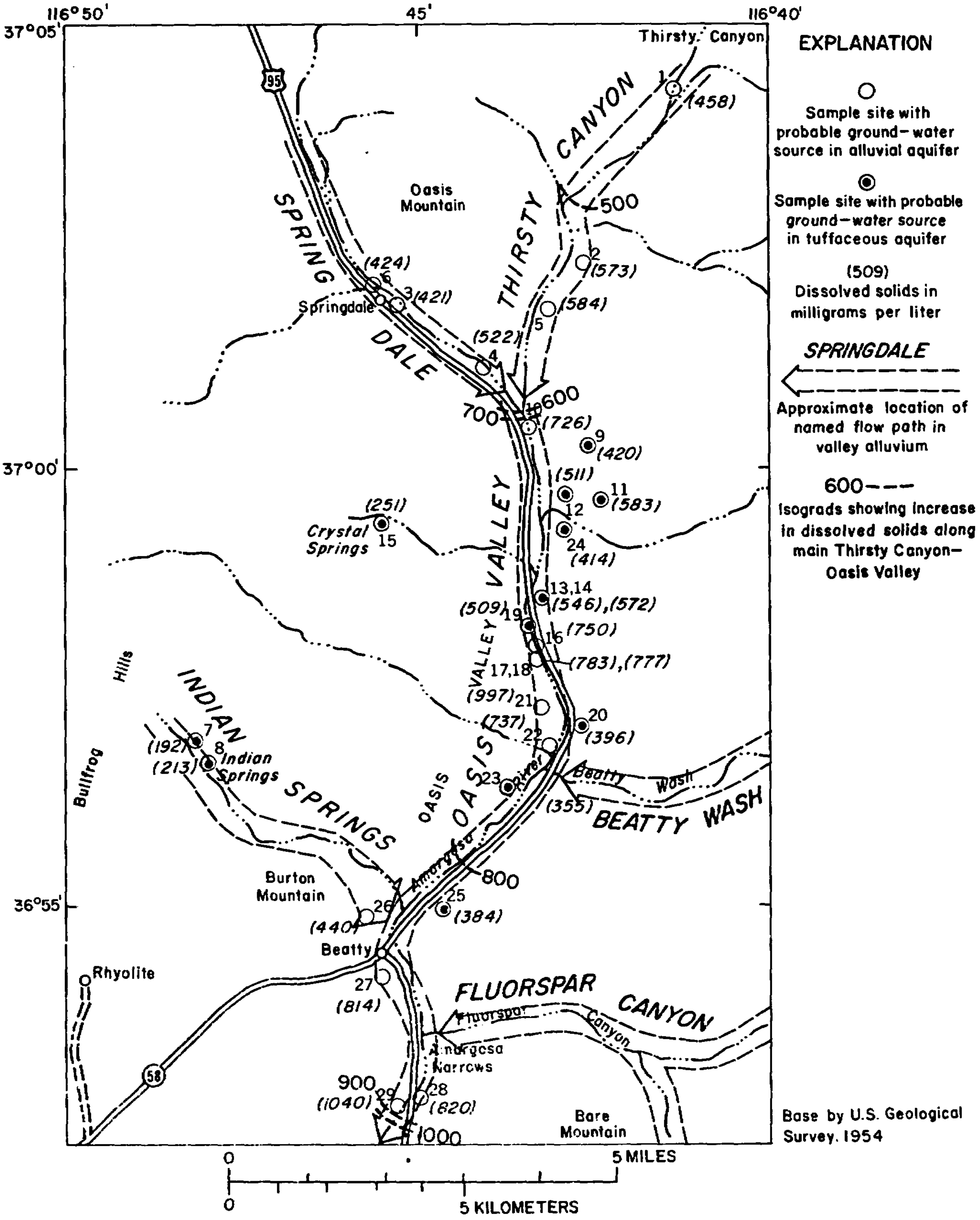


FIGURE 3.—The approximate locations of the ground-water flow paths in the alluvium and the regional distribution of dissolved solids in the alluvial and tuffaceous aquifers.

ters from Indian Springs and Crystal Springs (fig. 3) that are recharged locally from the Bullfrog Hills probably have relatively short residence times within the tuffaceous aquifer. Dissolved solids in these ground waters are considerably lower than they are in ground water issuing from springs along the east side of Oasis Valley. Ground water from the springs on the east probably has much more distant recharge areas within the tuffaceous aquifer to the north and east of Oasis Valley.

The second stage in the geochemical history of Oasis Valley is the upward percolation of ground water by subsurface flow into the shallow alluvial aquifer. Figure 3 shows that the concentration of dissolved solids increases progressively along the main Thirsty Canyon-Oasis Valley flow path. Ground water in the alluvium at site 1, the uppermost sampling point on the flow path, contains 458 mg/L dissolved solids. Ground water in the alluvium at the lower end of the flow path contains 1,040 mg/L dissolved solids or more than twice the amount contained at site 1. Although some additional reaction may occur between the ground water and tuffaceous detritus in the alluvium, the principal mechanism appears to be an increase in chemical concentration caused by a decrease in the volume of ground water owing to the immediate proximity of the water table to the atmosphere and soil zone. The decrease is probably the result of both direct evaporation and transpiration through the vegetation cover.

CHEMICAL CHARACTERISTICS CONTROLLED BY THE TUFFACEOUS AQUIFER

Although much of the ground water in the alluvium may have undergone concentration increases and reactions due to evapotranspiration, the chemical composition of all ground water in Oasis Valley is assumed to generally reflect a solute composition determined by interaction with solid phases of the tuffaceous rock. This interaction consists of dissolution and hydrolysis of primary mineral phases and precipitation of secondary minerals.

EQUILIBRIUM RELATIONSHIPS

The percentages of primary mineral phases vary in the tuffs with changes in bulk chemistry and in degree of devitrification. The most common minerals are glass, alkali feldspar, plagioclase, quartz; lesser amounts of biotite, clinopyroxene, and opaque oxide occur (Cornwall and Kleinhampl, 1964; Lipman, and others 1966). The principal alteration minerals, which formed as a result of ground-water action, include clay minerals, zeolites, cristobalite, and possibly potassium feldspar. The clay minerals are principally montmorillonite and montmorillonite-illite mixed-layer clays. The zeolites are primarily of the sodium-potassium types, dominantly clinoptilolite and analcime and, to a lesser extent, mordenite and chabazite (Hoover, 1968).

Table 4 shows the mean average thermodynamic saturation of both alluvial and tuffaceous ground waters with respect to a number of silicate minerals observed in the tuffaceous rocks of Oasis Valley. The term, IAP/K_S, defines the ratio of the actual aqueous ionic activities products (IAP) to the expected solubility products in equilibrium with a given mineral phase (K_S). If IAP/K_S is less than unity, the ground water is undersaturated and will tend to dissolve a particular phase. If IAP/K_S is greater than unity, the water is supersaturated and may tend to precipitate a given phase out of solution. Whether a mineral does indeed form depends both on its stability with respect to other minerals and kinetic factors influencing nucleation and precipitation. The ground water is supersaturated with respect to the potassium feldspar, adularia, which has been observed as a ground-water alteration product (Hoover, 1968). The water is undersaturated in relation to albite and anorthite, and two end members of the plagioclase solid solution. Plagioclase is found only as a primary mineral. The ground water is also supersaturated in terms of three clay minerals; kaolinite, montmorillonite, and illite. The aqueous silica concentration displays near-saturation with respect to silica gel and supersaturation with respect to both cristobalite and quartz. Although data is not given in table 4, several of the springs emanating from tuffaceous rocks in the east central part of Oasis Valley are also saturated with calcite.

Table 4 is incomplete owing to the lack of thermodynamic data for a number of zeolite phases. Analcime, one zeolite for which solubility data exist, is undersaturated by more than two orders of magnitude. Such a high degree of undersaturation is of interest because analcime occurs extensively in some altered tuffs adjacent to Oasis Valley to the north and east (Hoover, 1968). Lack of saturation suggests that ongoing zeolitization, as documented by Benson (1978),

TABLE 4.—*Comparison between mean ionic-activity products of Oasis Valley ground water and solubility products of selected silicate phases*

Mineral	Ionic Activity Product (IAP)	Solubility Product (K_S) at 25°C	IAP/K_S
Adularia	1.2×10^{-20}	2.7×10^{-21}	4.4
Albite	5.2×10^{-19}	1.0×10^{-18}	.52
Anorthite	9.8×10^{-22}	3.8×10^{-20}	.026
Kaolinite	2.0×10^{-37}	1.2×10^{-37}	1.7
Montmorillonite	5.0×10^{-28}	2.0×10^{-30}	250
Illite	3.8×10^{-40}	5.4×10^{-41}	7.0
Potassium-Mica	5.5×10^{-51}	7.9×10^{-50}	.070
Analcime	1.6×10^{-15}	2.0×10^{-13}	.0080
Silica gel	9.1×10^{-4}	9.6×10^{-4}	.95
Cristobalite	9.1×10^{-4}	2.6×10^{-4}	3.5
Quartz	9.1×10^{-4}	9.9×10^{-5}	9.2

probably occurs in localized geochemical environments that are not reflected in the average composition of ground water entering Oasis Valley. The existence of such localized environments is supported by the work of Gibbons, Hinrichs, and Botinelly (1960), who found that many of the zeolites in southern Nevada occur above clay zones and some densely welded tuffs. These workers suggest that the confining effect of impermeable layers slow the rate of flushing of solute species from the aquifer. The increase in aqueous concentrations as a result of continuing reaction with the tuffaceous rocks causes zeolitization. At least in the case of analcime, most of the ground water contained in Oasis Valley never reaches a composition that permits zeolitization.

Although individual minerals listed in table 4 may be saturated or supersaturated with respect to the ground water, their existence in the natural system is not guaranteed because stability with respect to other solid phases is not considered. Activity diagrams developed by Garrels and Christ (1965), Helgeson, Brown, and Leeper (1969), and other workers depict the stability fields of mineral species coexisting with varying aqueous solutions. Compositions for the Oasis Valley ground water are plotted for the systems $K_2O - MgO - H_2O - Al_2O_3$, $Na_2O - MgO - H_2O - Al_2O_3$, and $CaO - MgO - H_2O - Al_2O_3$ in figure 4. Such stability diagrams are based on the free energy of formation for each solid phase considered.

Previous literature has cited the free-energy data for montmorillonite as estimated through indirect means by Helgeson (1969), Hemley, Meyer, and Richter (1961) and Marshall (1949). Those estimates were based on the assumption that the stability of montmorillonite is dependent on the nature of the absorbed ion (i.e., sodium montmorillonite, calcium montmorillonite, etc.). Recently, Kittrick (1971a, b) has shown that the solubility of montmorillonite depends upon ions common to the crystal structure and upon the magnitude of the exchange capacity, but it is independent of the type of exchangeable ion and its activity in solution. Kittrick measured experimentally the free energy of formation and the solubility products for montmorillonites from Aberdeen, Mississippi, and Belle Fourche, South Dakota. Table 5 shows selected chemical components normalized to silica for Kittrick's montmorillonites and two montmorillonites that occur in or adjacent to Oasis Valley; the latter are from the Grouse Canyon Member of the Belted Range Tuff (Indian Trial Formation of former usage) and the Ammonia Tanks Member of the Timber Mountain Tuff (Carr, 1974). The principal variations present in table 5 are due to substitutions of magnesium and iron for aluminum in the octahedral coordination sites and the replacement of silica by aluminum in the tetrahedral sites. These substitutions are responsible for the charge imbalance which is neutralized by absorbed cations. A comparison between the montmorillonite from Aberdeen, Mississippi (Kittrick, 1971a, b) and the montmorillonites of the Grouse Canyon and Ammonia Tanks Members show that aluminum and magnesium are only slightly deficient in the latter samples. This deficiency may be partly due to the presence of unaltered silica glass in the samples. Montmorillonites of the Grouse Canyon and Ammonia Tanks Members show less iron by a factor of two in comparison to the Aberdeen sample. If montmorillonites of the Grouse Canyon and Ammonia Tanks Members represent the average composition of montmorillonite formed by Oasis Valley ground water, an assumption must be made that the substitution between aluminum and iron in the quantities shown in table 5 does not affect the free energy of formation of the Aberdeen montmorillonite. The degree of magnesium substitution in the montmorillonites of the Grouse Canyon and Ammonia Tanks Members is assumed to be equal to that found in the Aberdeen montmorillonite. A decrease in the iron concentration is balanced by an increase in aluminum. The charged montmorillonite structure is assumed to be balanced by hydrogen-ion absorption which permits expression of the chemical activities as ratios in terms of hydrogen-ion activities. Because the type of adsorbed cation does not greatly affect the free energy of formation of the montmorillonite structure (Kittrick, 1971a, b), the exchange of hydrogen ion for sodium, potassium, or calcium should not significantly change the stability relations. The equation below, which defines the stability boundary between a montmorillonite of the average composition of samples from the Grouse Canyon and Ammonia Tanks Members and potassium feldspar, is used as an example. An equilibrium expression between the two minerals can be written in terms of the logarithms of the aqueous and solid activities and an equilibrium constant.

$$\begin{aligned}&6.31 \log a_{KAlSi_3O_8\,(\text{feldspar})} + \log a_{H^+} + 0.61 \log a_{Fe^{+++}}\\&+ 1.73 \log a_{Mg^{++}} + 12.61 \log a_{H_2O} - 6.31 \log a_{K^+}\\&- 4.25 \log a_{H_4SiO_4}\\&- 3.81 \log a_{H_{.42}Mg_{.45}Fe_{.16}Al_{1.45}Si_{3.82}O_{10}(OH)_2}\\&(\text{Montmorillonite}) = 1\,688\end{aligned}$$

The expression on the right hand side of the equation is the logarithm of the equilibrium constant. Assuming that the activities of the solid phases and water are unity, the above expression can be rearranged to give:

$$\begin{aligned}&1.73 \log \frac{a_{Mg^{++}}}{a^2_{H^+}} + 0.61 \log \frac{a_{Fe^{+++}}}{a^3_{H^+}} - 6.31 \log \frac{a_{K^+}}{a_{H^+}}\\&\qquad - 4.23 \log a_{H_4SiO_4} = 1.688\end{aligned}$$

In the above equation as well as in the other stability expressions, the iron-to-hydrogen activity ratio and the silica activity are assumed to equal constants defined by the average solute concentrations of the Oasis Valley ground water. Substituting 17.66 for log $\frac{a_{Fe^{+++}}}{a^3_{H^+}}$ and -3.04 for log $a_{H_4SiO_4}$ into the above equation gives the relationship:

$$1.73\log\frac{a_{Mg^{++}}}{a^2_{H^+}} - 6.31\log\frac{a_{K^+}}{a_{H^+}} = 21.943.$$

Variables in this equation are defined as coordinates in the first diagram of figure 4A. The resulting linear plot represents the stability boundary between montmorillonite and adularia as a function of varying magnesium, sodium, and hydrogen activities. Other stability boundaries shown in figure 4 are derived in an analogous manner.

TABLE 5.—*Comparisons of selected chemical components normalized to silica for montmorillonites from tuffaceous rocks that are used in stability calculations*

Montmorillonites	atoms per unit cell			
	Mg	Fe	Al	Si
Aberdeen, Miss[1]	0.45	0.34	1.49	3.82
Belle Fourche, S. D.[2]	.28	.23	1.53	3.82
Oasis Valley, Nev.[3]:				
Grouse Canyon Member of the Belted Range Tuff	.42	.17	1.39	3.82
Ammonia Tanks Member of the Timber Mountain Tuff	.38	.14	1.29	3.82

[1] Kittrick, 1971b.
[2] Kittrick, 1971a.
[3] Carr, 1974.

Solid lines in figure 4 define the stability field for a montmorillonite with an iron concentration equal to the average concentration found in the montmorillonites of the Grouse Canyon and Ammonia Tanks Members. The more extensive montmorillonite-stability field represented by dashed lines is for an iron concentration equivalent to the Aberdeen montmorillonite while the smaller field defined by dashed and dotted lines is for a montmorillonite that contains no iron. At a specific aqueous-iron concentration, the stability fields of montmorillonites containing succes-

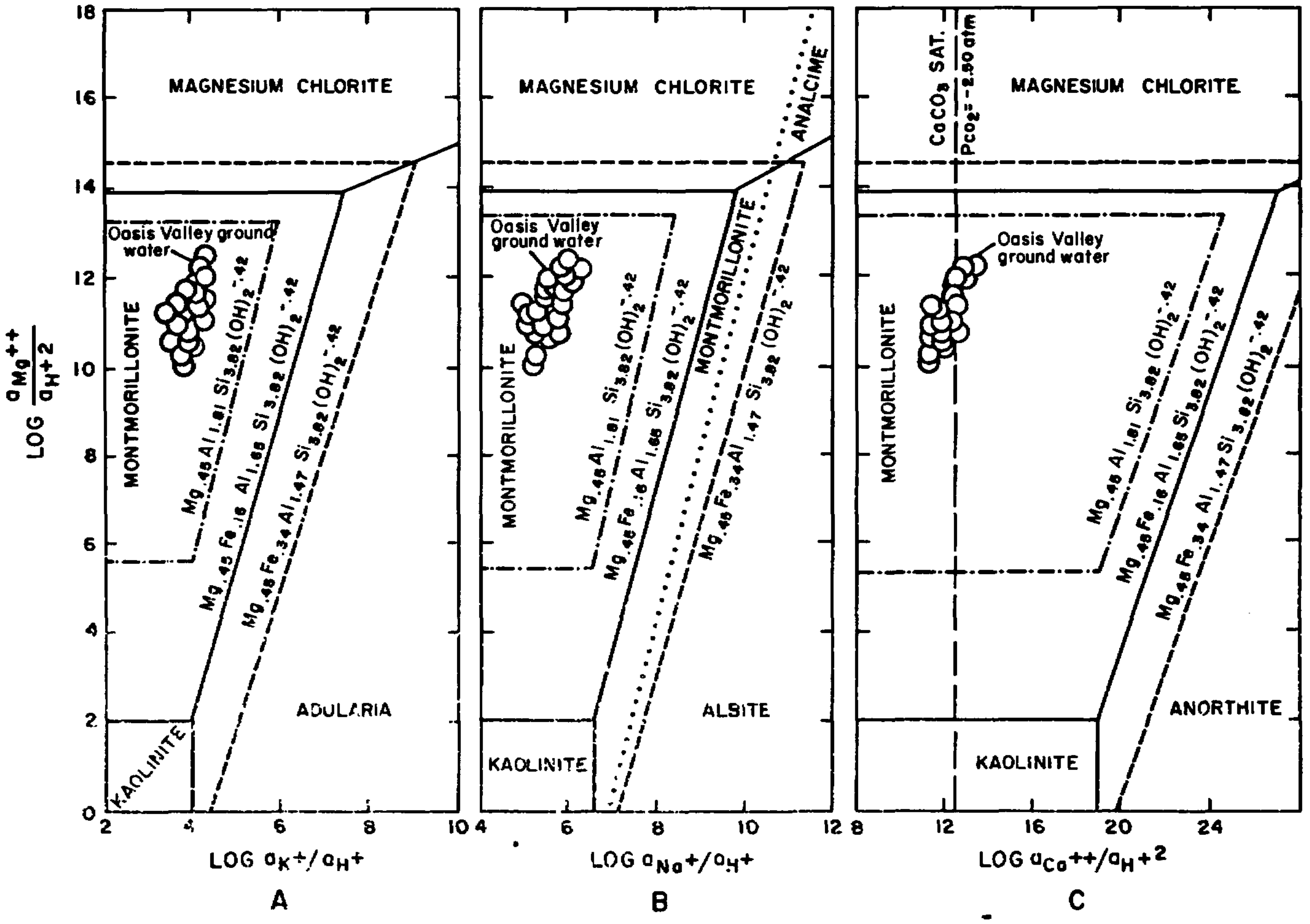


FIGURE 4.—Aqueous activity diagrams depicting montmorillonite stability.

sively more iron expand at the expense of other minerals that do not contain iron.

Regardless of the lattice-iron concentrations, however, figure 4 depicts montmorillonite as the stable phase in equilibrium with Oasis Valley ground water. The stability of montmorillonite as a weathering product is documented by its occurrence in the tuffs surrounding Oasis Valley as well as in other tuffaceous rocks (Sheppard and Gude, 1968, 1973). Kaolinite occurs at lower ionic-activity ratios (fig. 4), and illite is unstable under all the conditions shown in the diagrams. Some of the clays in the tuff formations of Oasis Valley are described as mixed-layer minerals which represent a presumably continuous gradation between montmorillonite and illite. Reliable thermodynamic data exist only for the two end-member clay minerals; therefore, stability fields for mixed-layer clays, though not shown in figure 4, may represent stable phases.

Because of the lack of thermodynamic data, the stability fields for a number of zeolites commonly found in the tuffaceous rocks surrounding Oasis Valley (Hoover, 1968) are missing from the diagrams. The metastable boundary between analcime, the only zeolite for which data exist, and an iron-free montmorillonite is shown for the $Na_2O - MgO - H_2O - Al_2O_3$ system in figure 4 as a dotted line.

Other zeolites such as clinoptilolite and mordenite have higher ratios of silica to aluminum in their structures than does analcime. These zeolites would have stability boundaries with slopes similar to that of analcime, but because of the relatively high silica concentrations found in Oasis Valley ground water, the boundaries would be shifted toward the upper left-hand corner of the diagrams in figure 4. These boundaries may encroach upon the montmorillonite stability field. The metastable analcime-montmorillonite boundary qualitatively demonstrates that water containing moderate amounts of magnesium leads to montmorillonite formation, whereas water containing sodium and potassium but deficient in magnesium favors analcime, clinoptilolite, and mordenite formation. Some water samples taken from tunnels driven into zeolitic tuffs at the adjacent Nevada Test Site have very low concentrations ($<5\times10^{-6}$ moles/liter) of magnesium and may be in equilibrium with respect to zeolite minerals.

The variability in hydrogen activities appears to be a controlling factor in the linear data distributions for Oasis Valley ground water shown in figure 4. This dependency is only apparent because the maximum and minimum activities of magnesium, sodium, and potassium, when divided by hydrogen activities, do not necessarily correspond to maximum and minimum ratios shown in the stability diagrams. Also, the distribution of data in the magnesium-sodium system, and to a lesser extent in the magnesium-potassium system, have slopes of approximately 2 to 1. These slopes are the same as the logarithmic ratio of hydrogen activities that occur in the denominators of the two coordinates, log $a_{Mg^{++}}/a^2_{H^+}$ versus log a_{Na^+}/a_{H^+} and of the coordinates, log $a_{Mg^{++}}/a^2_{H^+}$ versus log a_{K^+}/a_{H^+}. This variability in hydrogen-ion activities is expected because ground water in the alluvium is subjected to varying degrees of atmospheric and soil-zone interactions that affect the carbon-dioxide partial pressures and the pH. The distribution of data in the magnesium-calcium system, as shown in figure 4C, is controlled principally by equilibrium with calcite.

SOURCES OF DISSOLVED SPECIES

SILICA

As shown by the equilibrium data in table 3, the aqueous concentration of silica is apparently controlled by equilibrium with silica gel. This relationship is supported by silica gel observed in fractures in tuffaceous rocks. From thermodynamic considerations, silica gel represents a metastable phase in relation to both quartz and cristobalite. Secondary low cristobalite and quartz (Ransome, and others, 1910; Hoover, 1968) within the groundmass and fractures of the tuffs probably represent subsequent crystallization of silica gel.

A median value for silica concentrations in ground water is 0.6 millimole per liter (Davis, 1964) compared with the average concentration of 2.5 millimoles per liter silica in Oasis Valley ground water. Similarly high concentrations are found in ground water derived from other tuffaceous rocks (White and others, 1963).

The principal silicate phases that are present in the tuffs and that could be adequate sources for silica are feldspars, quartz, and volcanic glass. Feth, Roberson, and Polzer (1964) showed that the principal source of silica in ground water from granitic rocks in the Sierra Nevada, the bulk chemical composition of which is similar to the tuffs, was the dissolution of plagioclase and, to a lesser extent, of potassium feldspar. The silica concentration of these waters averaged one-third of the concentrations found in the Oasis Valley ground water. This difference suggests that volcanic glass and not feldspars is the major contributor of high silica concentrations in the Oasis Valley ground water. Jones (1966) and other workers have recognized that glasses, which are much more soluble than crystalline silicate minerals, can produce high silica concentrations in ground water.

Water can alter volcanic glass by hydration and leaching. Both of these processes can contribute silica to the aqueous system. Assuming constant aluminum concentrations, Lipman (1965) estimated that volcanic glass in the tuffs of southern Nevada had been leached of several percent more silica than had the crystalline rocks of the same composition and origin.

SODIUM, POTASSIUM, CALCIUM, AND MAGNESIUM

The source of the major cations in the ground water in the tuffaceous aquifer must be potassium-feldspar, plagioclase, and volcanic glass. Comparison between Oasis Valley ground water and water derived from the springs in Sierra Nevada rocks with about the same bulk composition (Feth, and others, 1964) shows a major difference in solute compositions. In the case of water from the granitic terrane, sodium and calcium are roughly equal as dominant ions whereas water from the Nevada tuffs exhibits a sole dominance of sodium, which comprises roughly 90 percent of the cations present.

The dissolution of plagioclase in the granitic rocks of the Sierra Nevada is well documented as the prime source of aqueous sodium and calcium by Garrels and MacKenzie (1967). Although the plagioclase in the tuffaceous rocks is slightly deficient in calcium ($AN_{25}-AN_{30}$) as compared with the plagioclase in the granitic rocks ($AN_{26}-AN_{40}$), breakdown of plagioclase is unlikely to produce the much higher sodium-to-calcium ratios found in Oasis Valley ground water.

A major source of high aqueous sodium concentrations appears to be volcanic glass. Table 6 shows a comparison between the relative molar percentages of sodium, potassium, calcium, and magnesium found in the glass and aqueous phases. The composition of the glass represents an average of three analyses reported by Lipman (1965) for tuff formations found in or around Oasis Valley. The aqueous composition is the average analyses for ground water in the tuffaceous aquifer of Oasis Valley not saturated with respect to calcite.

As is apparent from table 6, the Oasis Valley ground water cannot be described by a simple congruent dissolution of the glass phase. The percent of sodium is increased by a factor of two in the aqueous state, magnesium is decreased by a factor of two, and potassium is decreased by a factor of fourteen.

Relationships between the glass and aqueous phases shown in table 6 have been predicted by other workers. Lipman (1965), in a chemical comparison of volcanic rocks of southern Nevada, showed that hydrated glasses are characterized by higher K_2O/Na_2O ratios than crystallized rocks. As an approximation, Lipman suggested that about 0.5 percent Na_2O has been removed by hydration and leaching of the glass phase while K_2O remains relatively immobile. Truesdell (1966) determined the ionic-exchange constants of several natural and synthetic glasses by use of an electrode method, and he found that glasses preferentially absorbed hydrogen, potassium, and, to a lesser extent, calcium relative to sodium. He predicted that waters in the vitric tuffs would be sodium-rich.

TABLE 6.—*Comparisons of relative molar percentages of selected cations found in the volcanic glass and Oasis Valley ground water*

	Volcanic glass[1]	Ground water[2]
Ca	8	8
Na	46	87
Mg	4	2
K	42	3

[1] Average of three analyses (Lipman, 1965) for tuffs in or around Oasis Valley.
[2] Average of all water analyses (this paper).

BICARBONATE

The dominant anion present in the tuffaceous aquifer is bicarbonate. The occurrence of carbonate minerals is minimal in the tuffaceous rocks (Lipman and others, 1966). The principal source and control of bicarbonate is the reaction of dissolved, soil-zone carbon dioxide with various mineral phases. In the case of glass, Budd (1961) has demonstrated that in neutral solutions similar to Oasis Valley ground water, electrophilic reactions occur in which hydrogen enters the glass structure as hydronium ion and exchanges with sodium or other cations bonded to lattice oxygen atoms. As hydrogen atoms are consumed in this exchange reaction, dissolved carbon dioxide will disassociate to produce bicarbonate ions.

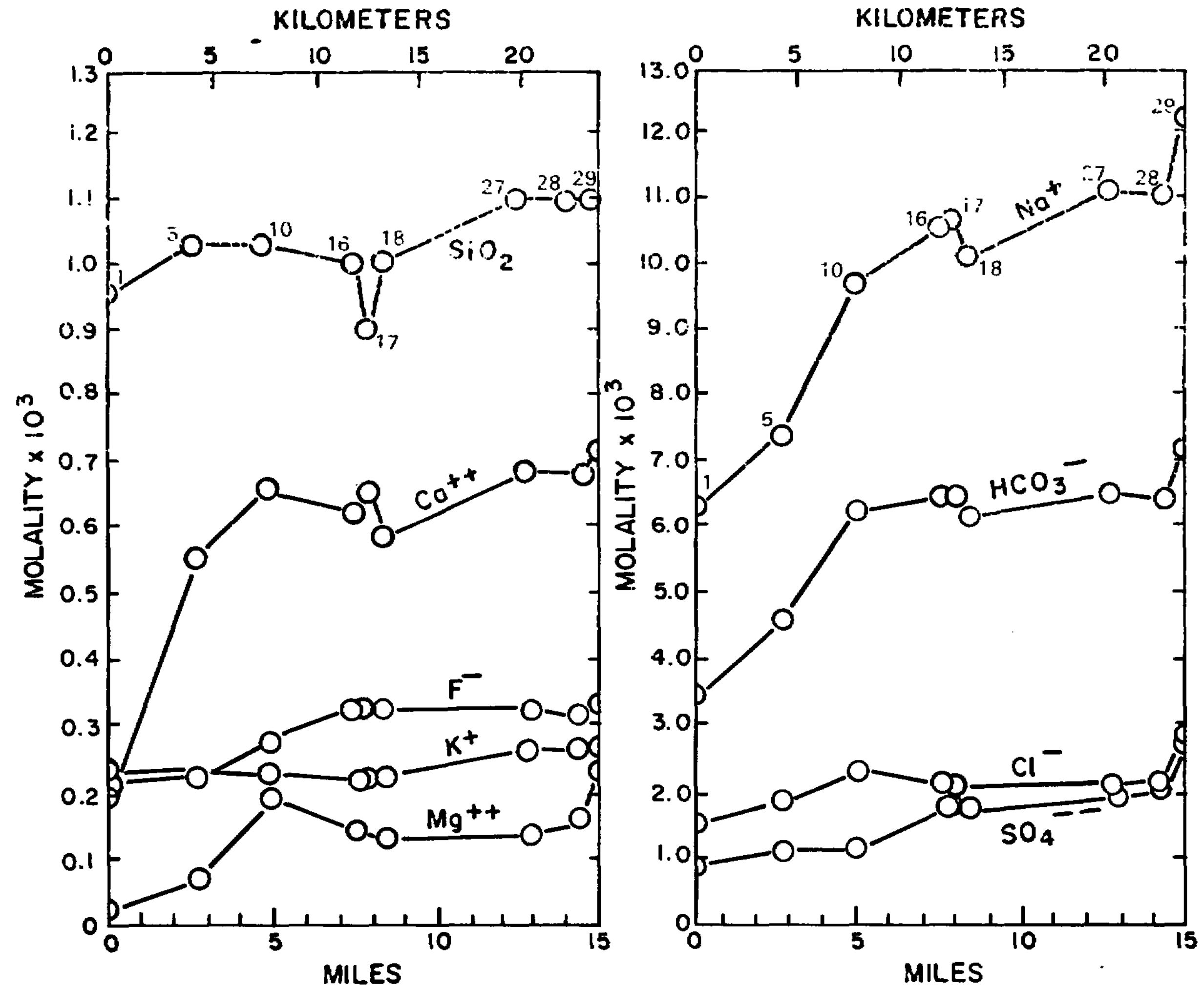
FLUORIDE AND CHLORIDE

Ratios of fluoride to chloride in tuffaceous rocks northeast of Oasis Valley vary between 0.5 and 2.0 (Noble and others, 1967). Ground water entering Oasis Valley through such rocks has ratios generally an order of magnitude less. This lack of fluoride mobility in comparison to chloride agrees with observations that, during alteration of volcanic glass, fluoride remains in the solid phase. Noble and others (1967) compared fluoride and chloride contents of a number of nonhydrated and hydrated glasses of the same origin and found that four-fifths of the chloride and less than half of the fluoride were lost during hydration.

CHEMICAL CHARACTERISTICS CONTROLLED BY THE ALLUVIAL AQUIFER

CONCENTRATION INCREASES

Figure 5 illustrates trends in concentration as a function of a distance of approximately 24 kilometers



Sample numbers are keyed to tables 1,2,and 3

FIGURE 5.—Changes in concentration of dissolved chemical constituents as a function of distance along the alluvial flow path.

(15 miles) along the Thirsty Canyon-Oasis Valley flow path. The data on the far left-hand side of the figure are from the northernmost sampling point (site 1) located near the mouth of Thirsty Canyon. The data on the far right-hand side are from the southernmost point (site 29) in the flow path located at the outlet of the Amargosa Narrows.

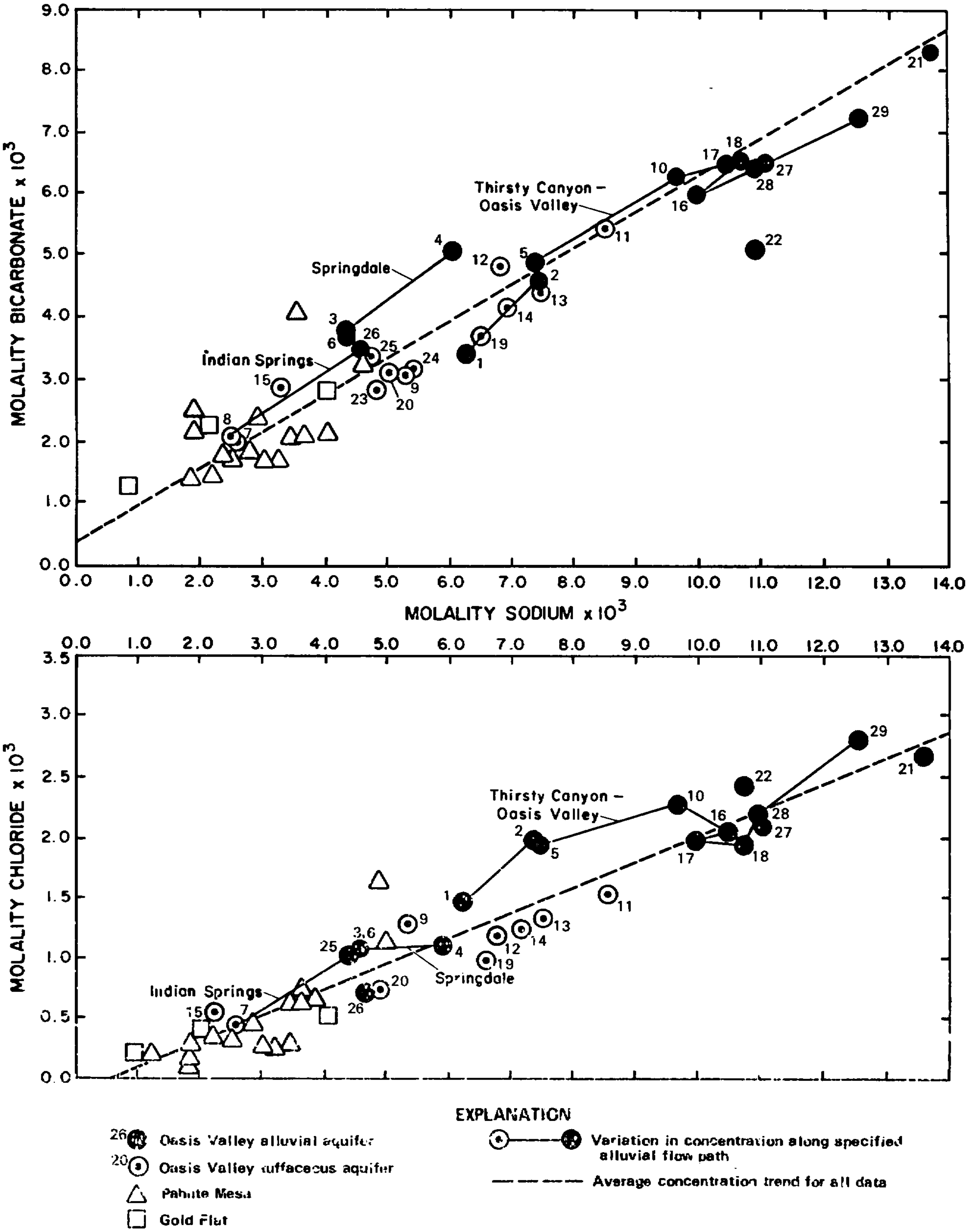
Sodium, bicarbonate, fluoride, and chloride show rapid increases in concentrations along the initial 8 kilometers (5 miles) of the flow path in the alluvium. Throughout the remaining distance, except for the final sampling point, these species show a more moderate increase. Calcium and magnesium display even greater concentration increases along the initial part of the flow path; silica and potassium show only minor enrichment.

RATIOS OF SOLUTE COMPONENTS

SODIUM, BICARBONATE, AND CHLORIDE

Figure 6 shows the aqueous concentrations of bicarbonate and chloride plotted against sodium. Included in the diagrams are data for ground water in the tuffaceous and alluvial aquifers of Oasis Valley. Numbered data points correspond to samples listed in tables 1, 2 and 3. Also shown in figure 6 are additional geochemical data for ground water from the tuffaceous aquifer under Pahute Mesa (Blankennagel and Weir, 1973) and Gold Flat (unpublished data from files of U.S. Geological Survey). The latter two areas represent probable recharge areas for Oasis Valley ground water.

The most significant observation is that nearly all the data presented in figure 6 plot on the same linear



Sample numbers are keyed to tables 1, 2, and 3

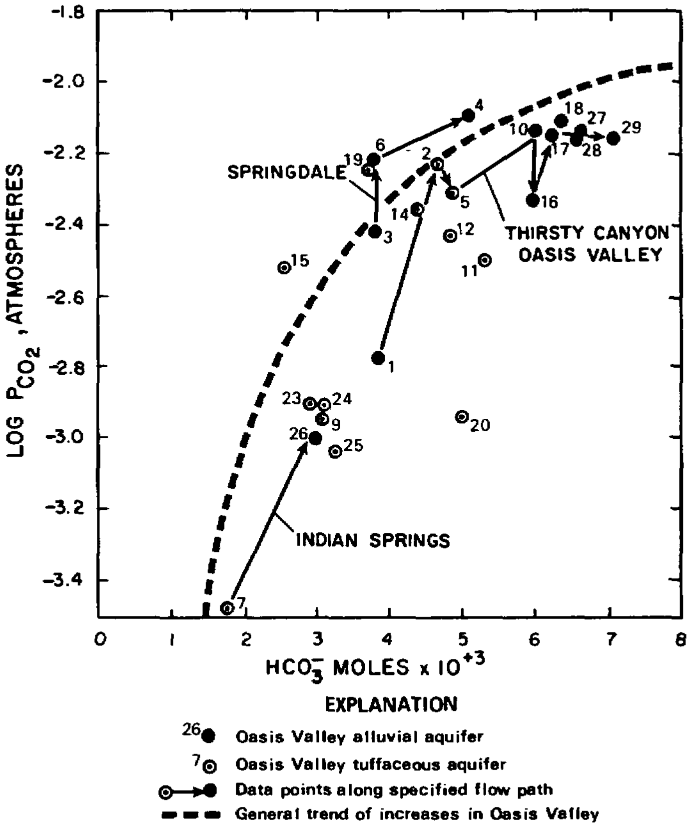
FIGURE 6.—Concentration trends of sodium, bicarbonate, and chloride.

trends. The data for the tuffaceous aquifer, both in the immediate vicinity of Oasis Valley as well as for Pahute Mesa and Gold Flat, plot in the more dilute region of the diagrams. Alluvial water compositions represented for specific flow paths in figure 6 range from overlapping the dilute region at the initial stages along the flow paths to considerably higher concentrations farther downgradient. The similarity in compositions supports the suggestion of Blankennagel and Weir (1973) that water beneath Pahute Mesa is chemically related to Oasis Valley ground water. The linearity of the data suggests that the water in the alluvium can be produced from tuffaceous compositions by concentration increases due to evapotranspiration. Sodium and chloride appear to be neither selectively added nor removed from the water during this process. Some variations in bicarbonate composition may be expected due to local dissolution or precipitation of carbonate minerals. The Springdale flow path appears anomalously high in bicarbonate, probably due to the dissolution of locally occurring Paleozoic carbonates (fig. 2). The slightly larger increase in bicarbonate along the initial part of the Thirsty Canyon-Oasis Valley system (fig. 6) may also represent dissolution of carbonate minerals in the alluvium, and the slight decrease along the final portion may represent precipitation after calcite saturation has been achieved. However, bicarbonate, like sodium and chloride, seems to be principally controlled initially by interaction with tuffaceous rocks and by later modification due to evapotranspiration.

Figure 7 shows the relationship between bicarbonate concentrations and the partial pressure of carbon dioxide in equilibrium with Oasis Valley ground water calculated from the expression

$$\log P_{CO_2} = \log a_{HCO_3} - \text{pH} - \log K_s$$

where $\log P_{CO_2}$ and $\log a_{HCO_3^-}$ are the logarithms of the partial pressure of carbon dioxide (P_{CO_2}) and the activity of bicarbonate respectively. Log K_s is the logarithm of the solubility constant. P_{CO_2} increases rapidly along the Thirsty Canyon-Oasis Valley and the Springdale flow paths relative to that associated with ground water in the tuffaceous aquifer. Increases in P_{CO_2} with increasing bicarbonate are reverse to the relationship previously discussed for the tuffaceous aquifer, in which bicarbonate is produced and CO_2 is consumed during the reaction with silicate minerals in a closed system. Rapid increases in dissolved CO_2 in the alluvial aquifer suggest that the hydrologic system interacts with the atmosphere through the root-zone transpiration of CO_2 by the relatively dense vegetation along the valley bottom.



Sample numbers are keyed to tables 1, 2, and 3

FIGURE 7.—Progressive increases in P_{CO_2} with increasing bicarbonate.

POTASSIUM AND FLUORIDE

Figure 8 shows the aqueous concentrations of potassium and fluoride plotted against sodium. No data exist for fluoride concentrations in ground waters of Pahute Mesa and Gold Flat. Both potassium and fluoride show concentration increases in the alluvial aquifer but at a progressively decreasing rate relative to sodium. Assuming that sodium concentration increases reflect relative volume decreases of ground water by evapotranspiration, the decrease of potassium and fluoride concentrations relative to sodium suggests that their absolute amounts in the aqueous system are being diminished.

The mechanism for the removal of potassium is not certain. Table 4 shows that the average aqueous system is saturated by a factor of more than two with respect to potassium feldspar. Proven difficulties in nucleation (Berner, 1971) plus the instability of potassium feldspar with respect to montmorillonite (fig. 4) tend to discount potassium feldspar as a likely sink for potassium. A possible mechanism for removing potassium is by absorption and incorporation into the lattice

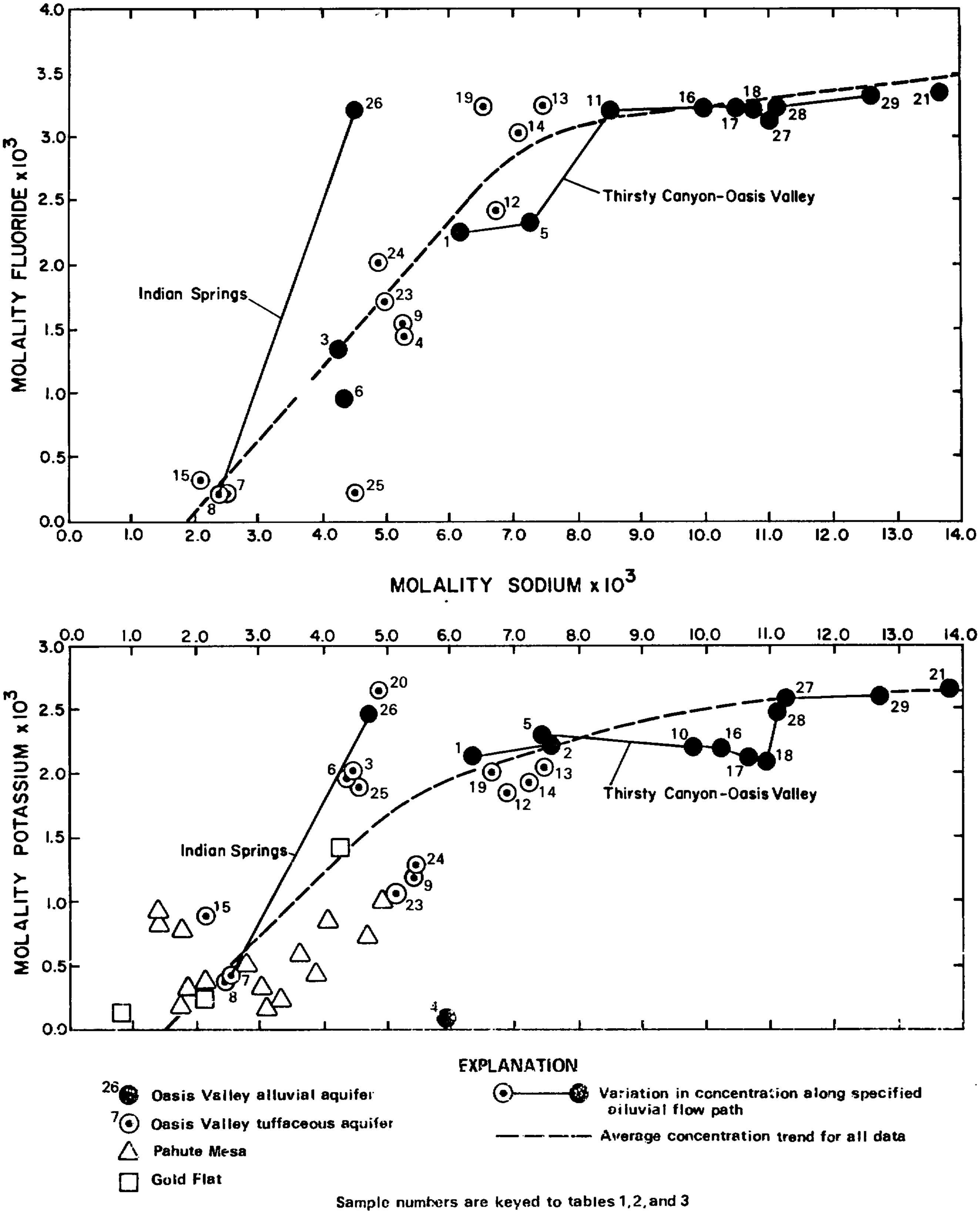


FIGURE 8.—Nonlinear average concentration trends of fluoride and potassium relative to sodium.

of clay minerals. Although large quantities of clay were deposited in the alluvium of Oasis Valley under subaerial and lacustrine conditions by erosion and weathering of the surrounding tuffs (Malmberg and Eakin, 1962), little is known concerning their specific mineralogy. However, degraded illites and montmorillonites, which are common clay minerals in most arid soil zones, adsorb and fix potassium. These minerals are known weathering products of the tuffs in and around Oasis Valley. Also the vegetation cover in Oasis Valley may remove significant amounts of potassium.

As will be shown in the section entitled "Equilibrium Relationships," the mineral fluorite appears to be the major sink for the removal of fluoride from the ground water in the alluvium.

CALCIUM AND SULFATE

Both calcium and sulfate show anomalous increases in relation to sodium, chloride, and bicarbonate that cannot be explained by increases due to evapotranspiration. Figure 9 shows the concentrations of calcium and sulfate plotted against sodium. Along the initial part of the main flow path labeled Thirsty Canyon-Oasis Valley, the calcium concentration increases by a factor of four, which is double the increase observed for sodium along the entire system. Figure 10 shows a comparison between calcium, sodium, and magnesium distributions for the Thirsty Canyon-Oasis Valley and Springdale flow paths. Even higher calcium percentages in the Springdale system are apparent. This high calcium content, coupled with the anomalously high bicarbonate-to-sodium ratios shown in figure 6, suggest that calcium carbonate is being dissolved in the Springdale system. The source of calcium carbonate is probably in the Bullfrog Hills. Carbonate rock crops out locally in the northern Bullfrog Hills west of Springdale. Ransome, Emmons, and Garrey (1910) also reported calcite in fractures and mineralized veins within the hydrothermally altered zones of the Bullfrog Hills. The calcite displays cavernous structure indicating dissolution by ground water. Elsewhere, such as in the Thirsty Canyon-Oasis Valley system, both calcium carbonate and calcium sulfate may occur in lacustrine beds within the alluvium.

The distribution of sulfate plotted against sodium is also shown in figure 9. The slope of the sulfate-to-sodium ratio is greatest in both the tuffaceous and alluvial aquifers of Oasis Valley relative to the Pahute Mesa and Gold Flats data. The slope is also greater for sulfate to sodium than for bicarbonate or chloride to sodium in the flow system in the alluvium. Like calcium, an additional source of sulfate must be contributed to the Oasis Valley ground water. Unlike calcium, however, figure 10 shows that the highest percentage of sulfate relative to bicarbonate and chloride in the alluvial aquifer is concentrated in the main Thirsty Canyon-Oasis Valley flow path.

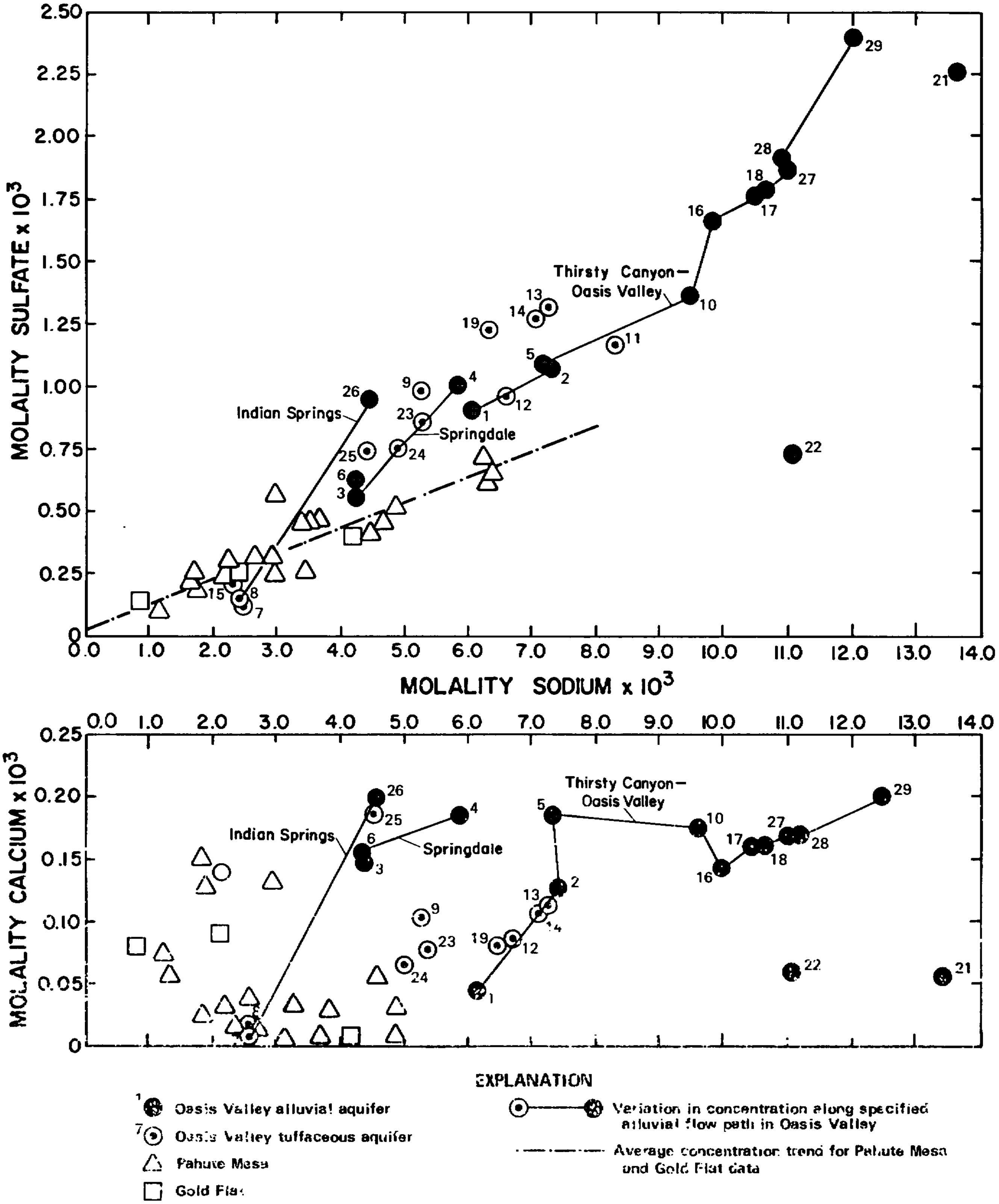
The primary source of most of the additional sulfate seems to be hydrothermal. Hot Springs (sample site 13), a major thermal (41°C) spring in the area, shows an abnormally high sulfate-to-chloride ratio. Also, the mineralogy of the hydrothermally altered tuffaceous rocks in the Bullfrog Hills suggests that sulfate may have been contributed locally from sulfide minerals. Although pyrite is not now abundant near the surface, the large amounts of limonite (Ransome and others, 1910) suggest that pyrite has been oxidized with the concurrent production of sulfate.

EQUILIBRIUM RELATIONSHIPS

As discussed in the section dealing with equilibrium relationships, the ground water in the tuffaceous aquifer is stable with respect to silica gel, montmorillonite, and possibly mixed-layer clay minerals. When the ground water moves from this aquifer into the alluvial fill of Oasis Valley, stability is maintained between this mineral assemblage and the aqueous phase. Silica concentrations remain constant throughout the flow system in the alluvium and appear to be continually controlled by silica-gel equilibrium. Montmorillonite stability appears to be maintained with increasing solute concentrations as the reaction paths advance across the montmorillonite stability field toward the chlorite boundary (fig. 4).

However, increasing chemical concentrations in the ground water of the Oasis Valley alluvium produce saturation with respect to several mineral phases in addition to those generally associated with the tuffaceous aquifer. Figure 11 shows the ionic-activity product of calcium fluoride plotted against the ionic-activity product of calcium carbonate. The figure also includes the stability fields for calcite and fluorite. Fluorite solubility is that given by Smyshlyaev and Edeleva (1962). Note that all ground-water samples associated with the tuffaceous aquifer are undersaturated with respect to fluorite and that the majority of samples are undersaturated with respect to calcite. Those waters that are calcite-saturated are confined to springs emanating along the east-central side of Oasis Valley and may be associated with carbonate deposition during local hydrothermal alteration of the tuffaceous rocks (Ransome and others, 1910).

Ionic-activity products for both calcium carbonate and calcium fluoride become progressively greater



Sample numbers are keyed to tables 1,2,and 3

FIGURE 9.—Average concentration trends of sulfate and calcium relative to sodium.

downgradient along the Thirsty Canyon-Oasis Valley and Indian Springs alluvial flow paths. Ionic-activity products increase until they intersect the stability fields of both calcite and fluorite. Beyond this point in the flow path, the ground water shows only minor and erratic variations in the ionic-activity products. This would indicate that calcium carbonate and calcium fluoride are being precipitated from the alluvial system as the volume of ground water is being reduced by evapotranspiration. Ground water originating from Indian Springs in the Bullfrog Hills shows a rapid increase in the ionic-activity product of calcium carbonate but only a minor increase in calcium fluoride. This

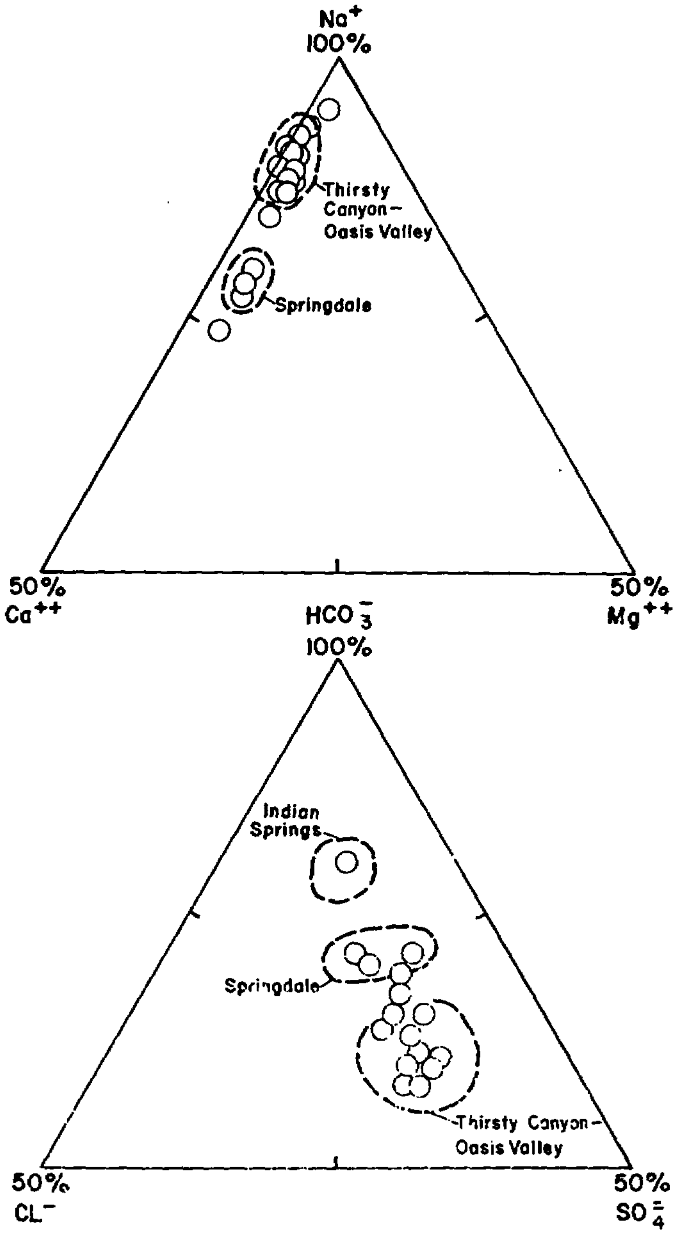


FIGURE 10.—Triangular diagrams depicting relative concentrations of selected cations and anions.

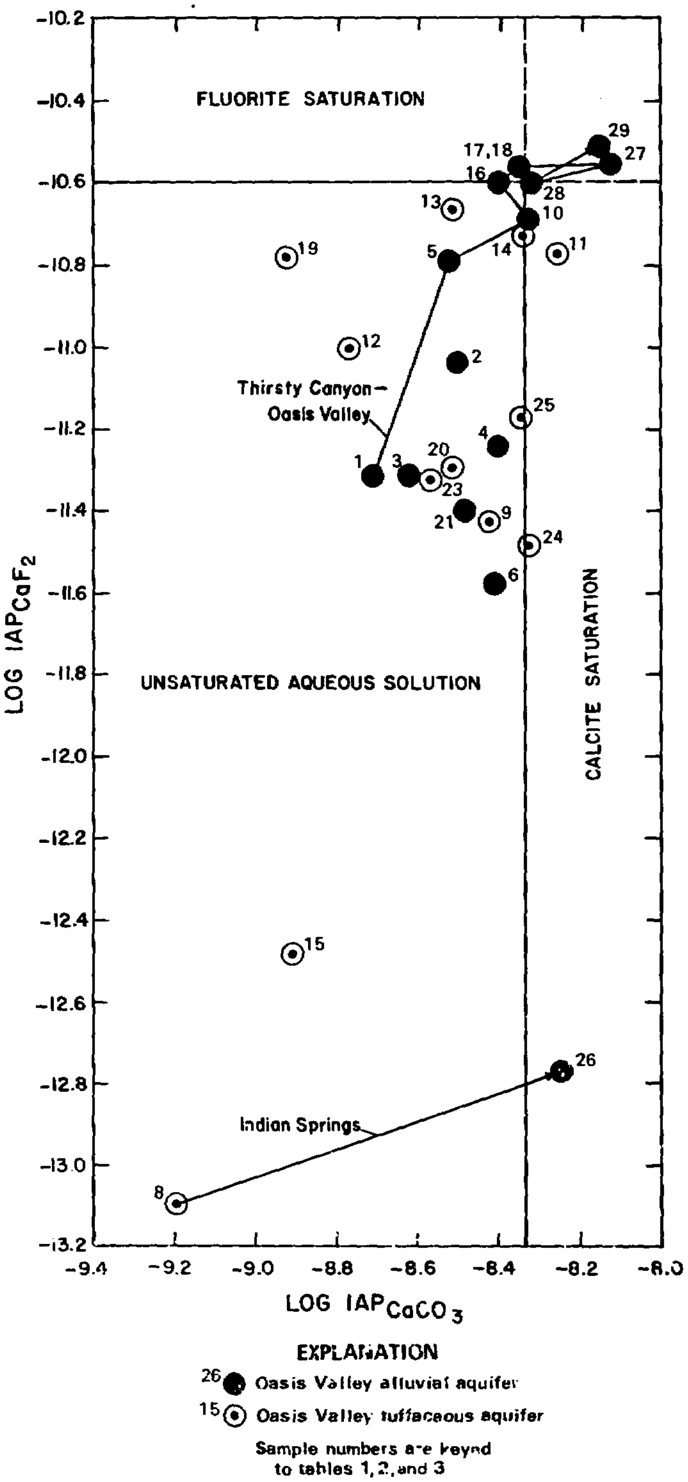


FIGURE 11.—Ionic-activity products of calcium fluoride compared to calcium carbonate. Saturation values are at 25°C.

rapid saturation with respect to calcite but not fluorite suggests again that calcium carbonate is being dissolved along the Indian Springs flow path.

Figure 12 shows the approximate geographic distribution of the saturation boundaries for calcite and fluorite. Equilibrium with respect to calcite occurs in the lower three-fourths of the main alluvial flow path that originates at the mouth of Thirsty Canyon. Equilibrium is also achieved throughout the Springdale flow path and the lower part of the Indian Springs flow path. Both of these systems have recharge areas in the Bullfrog Hills and show abnormally high calcium carbonate concentrations as compared with the dissolved-solids concentrations. Fluorite saturation is limited to a narrow strip in the lower center of the valley; it coincides with the area in which the ground water would be subjected to maximum evapotranspiration. Most of the springs issuing from the tuffaceous aquifer, with the exception of those in the central part of Oasis Valley, are not saturated with calcite or fluorite.

The concentration of aqueous magnesium also appears to be controlled by an equilibrium relationship although the exact mechanism is less well defined than for calcium and fluoride. Initially, the percentages of magnesium increase downgradient in the water in the alluvium at a much faster rate than do the percentages of sodium, chloride, and bicarbonate (fig. 5). This rapid increase suggests that, like calcium, magnesium is being added to the system from an additional source. Figure 13 shows the ionic-activity product of magnesium carbonate plotted against calcium carbonate. Included in the figure are the stability fields for calcite, magnesite, and dolomite. Both Thirsty Canyon and Indian Springs flow paths display initial rapid increases in the ionic-activity products of magnesium carbonate and calcium carbonate. However, both systems reach steady states downgradient, after which the ionic-activity products show only minor erratic increases and decreases. As in figure 11 for the calcium carbonate versus calcium fluoride system, such a steady-state situation suggests equilibrium conditions between aqueous and solid phases The limiting value for calcium carbonate activities is controlled by calcite equilibrium (fig. 11). The distribution of the data suggests that calcium carbonate and magnesium carbonate activities also approach the solubility of dolomite from undersaturation. The inability of many, even highly supersaturated, waters to precipitate dolomite is well documented (Berner, 1971). Therefore, dolomite precipitation as a means of controlling magnesium concentrations in saturated or near saturated systems such as Oasis Valley is very improbable. However, waters that are dissolving dolomites exhibit solute concentrations which approach saturation with respect to dolomite (Hem, 1970). Figure 13 suggests that the limiting value for magnesium concentrations in the Oasis Valley system is based on the ability of the ground water to dissolve dolomite. Once the system is almost saturated with dolomite, little more magnesium is introduced into the system. This theory implies that dolomite dissolution and not evapotranspiration is the dominant control on the maximum magnesium concentrations found along the flow paths in the alluvium. Dolomite crops out extensively in the hills southwest and southeast of Beatty and is present at depth under the Bullfrog Hills (Ransome and others, 1910). Oasis Valley ground water could come in contact with these rocks or with alluvium derived from them.

The Indian Springs system, which is initially greatly undersaturated with respect to both calcite and dolomite, shows a calcium to magnesium slope of 1 to 1 (fig. 13). This slope would be expected from a congruent dolomite dissolution. The Thirsty Canyon system is initially much closer to calcite saturation. If dolomite reacts similarly to magnesian calcites, as proposed by Plummer and Mackenzie (1974), dissolution becomes incongruent near calcite saturation. Incongruent dissolution produces dominantly aqueous magnesium carbonate. This mechanism would explain why the magnesium-to-calcium ratios in the Thirsty Canyon-Oasis Valley system are higher than those in the Indian Springs system.

MASS BALANCE OF CHEMICAL SPECIES

As a means of summarizing the behavior of aqueous chemical species in the alluvial aquifer, a mass balance comparison is made in table 7 between chemical compositions of ground water recharging and discharging the alluvium. Line 1 in table 7 lists the chemical composition of ground water at site 29 below the mouth of the Amargosa Narrows (fig. 2). Assuming that the Paleozoic carbonate basement within the Amargosa Narrows is relatively impermeable, all ground water discharging from the alluvium in Oasis Valley must pass through the 3–4 meter (9–12 ft) thickness of alluvium at this point Sample 29, immediately downgradient from the Amargosa Narrows should, therefore, be representative of the composition of ground water discharging the alluvium.

An estimate of the chemical composition of water recharging the alluvium from the tuffaceous aquifer is more difficult owing to the number of springs and seeps as well as probable subsurface flow. As discussed by Malmberg and Eakin (1964) and Blankennagel and Weir (1973), most ground water that recharges the alluvium probably moves considerable distances through the tuffaceous aquifer from areas north and east of

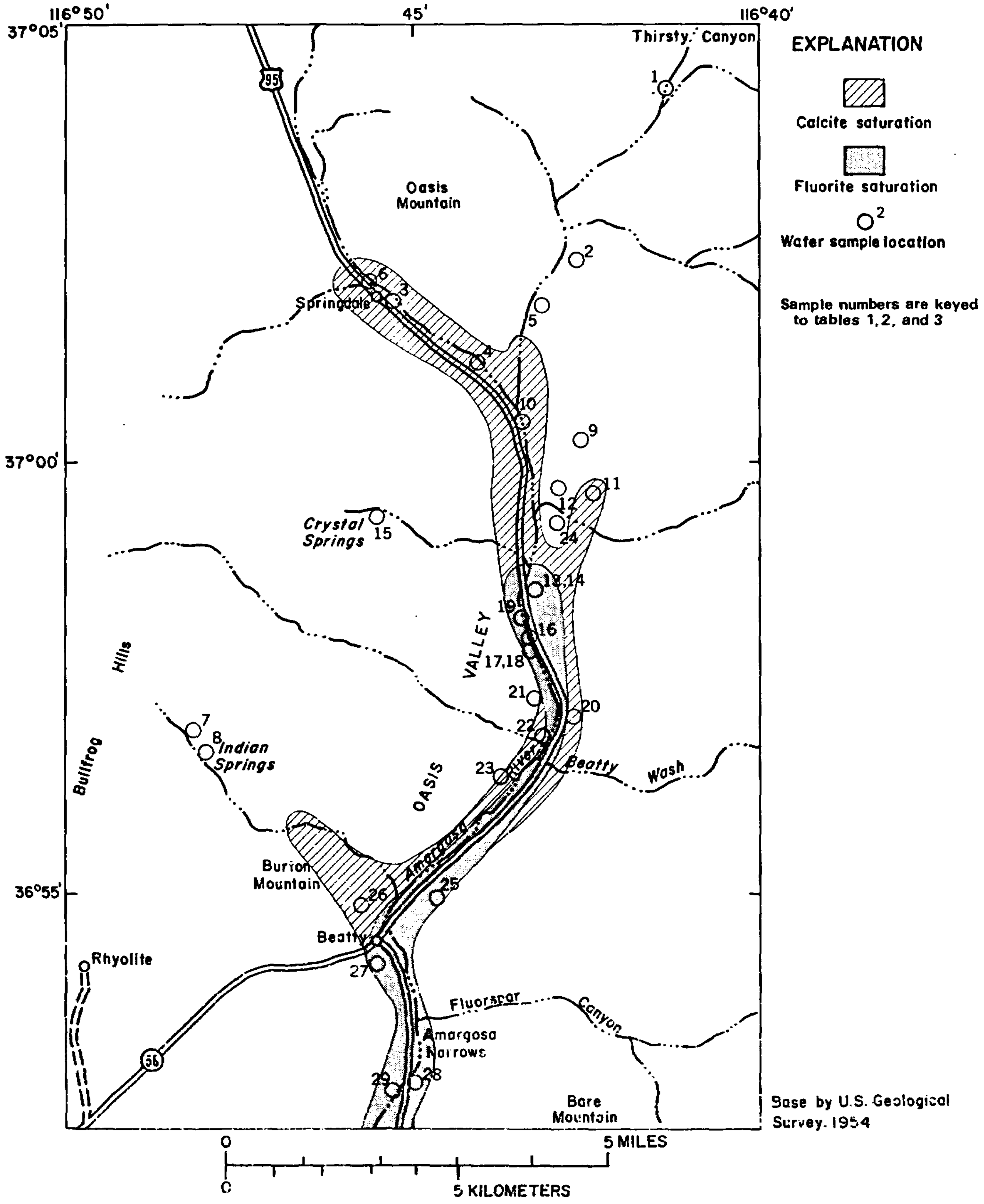


FIGURE 12.—Geographic distribution of calcite- and fluorite-saturated ground water.

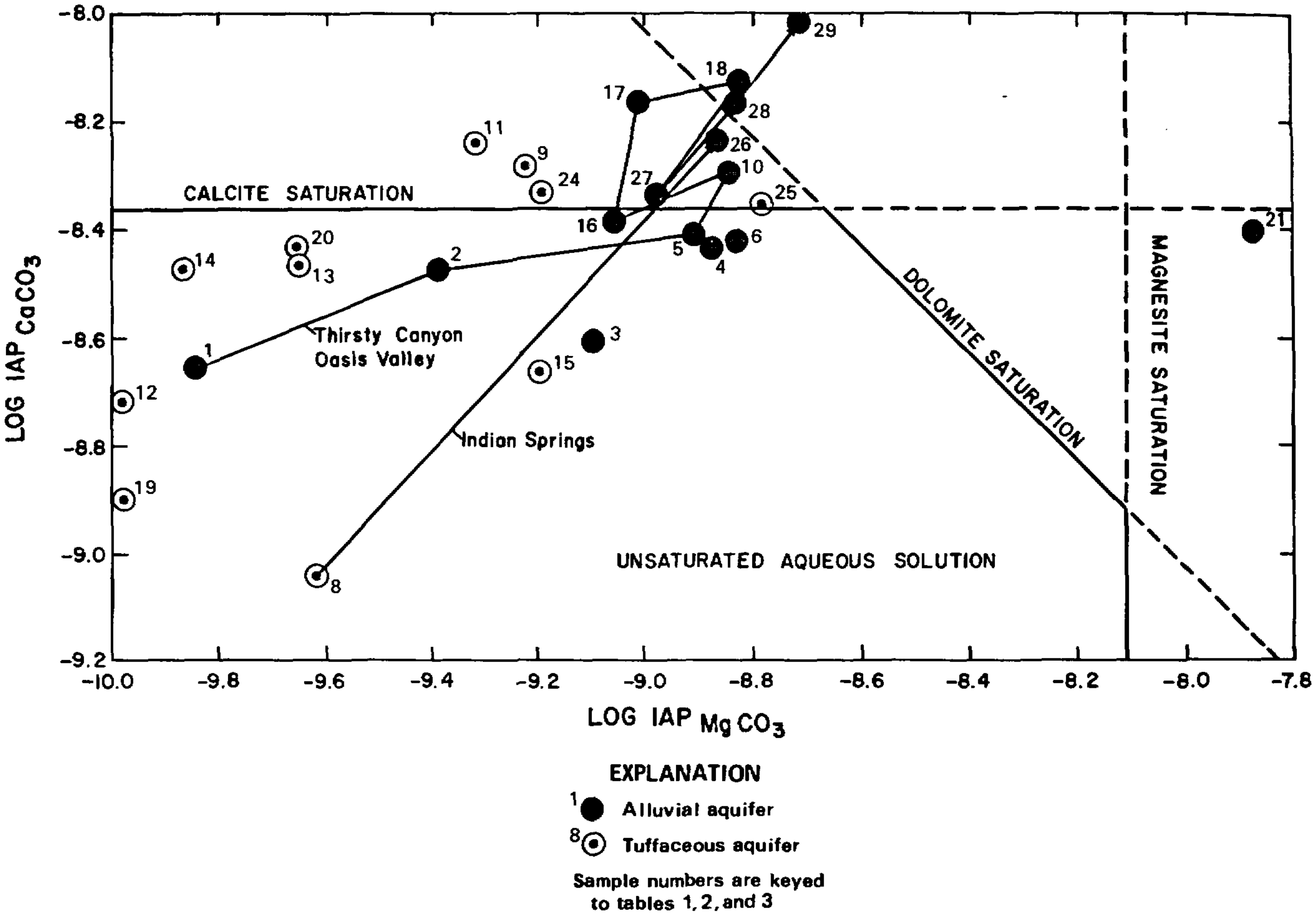


FIGURE 13.—Ionic-activity products of magnesium carbonate compared to calcium carbonate.

Oasis Valley. Chemical composition would be expected to be similar at individual points where this regional tuffaceous aquifer recharges the alluvium in Oasis Valley. The general similarity in chemical compositions of ground water in the tuffaceous aquifer is shown in table 2. The principal exceptions are samples 7, 8, and 9 from springs in tuffaceous rocks to the west of Oasis Valley (fig. 3) which represent local recharge from the Bullfrog Hills. The average composition of the remaining 11 water samples from the tuffaceous aquifer (table 3) is, therefore, assumed to represent the chemistry of water recharging the alluvium and is shown on line 2 in table 7.

In the preceding discussion of chemical behavior, sodium and chloride appeared to be the two species that were neither added to nor removed from the ground-water system in the alluvium. The increases in sodium and chloride concentrations between lines 1 and 2 in table 7 must, therefore, reflect the corresponding decrease in the volume of water as the result of evapotranspiration. Assuming a volume reduction of 2.13 overestimates the sodium-discharge concentration by 0.37 millimole (line 4), or 3 percent (line 5), and underestimates the chloride concentration by 0.11 millimole, or 4 percent.

Evapotranspiration probably affects only the shallow ground water directly adjacent to the root zone and atmospheric interface. However, chemical trends along the flow paths are preserved irrespective of the sampling depth (0–100 m, 0–300 ft, table 1). Dispersivity along the flow path apparently produces chemical homogeneity within the zone sampled. If the alluvium thickness is more than 660 m (2,000 ft) in the central part of Oasis Valley, as suggested by Malmberg and Eakin (1964), concentrations may be more dilute at greater depth. However, no mixing of more dilute ground water with the shallow alluvial water occurs as the flow system approaches the hydrologic constriction at the Amargosa Narrows. The mass-balance calculation involving only discharge of shallow ground water appears to describe the hydrologically-active system in the alluvium.

The estimate in this report that slightly more than half (53 percent) of the ground water contained in

TABLE 7.—*Comparisons of selected chemical species in ground water from the mouth of Thirsty Canyon and the exit of Amargosa Narrows*

[Constituents in millimoles per liter]

	Na^+	K^+	Ca^{++}	Mg^{++}	HCO_3^-	$SO_4^=$	Cl^-	F^-	H_4SiO_4
Water composition at Amargosa Narrows	12.62	0.26	0.95	0.23	7.20	2.60	2.82	0.33	1.12
Average water composition of tuffaceous aquifer[1]	6.10	.17	.45	.07	3.68	1.12	1.27	.24	.90
Average water composition of tuffaceous aquifer × 2.13	12.99	.36	.96	.15	7.84	2.39	2.71	.51	1.92
Molality difference[2]	– .37	– .10	– .01	+ .08	– .64	+ .21	+ .11	– .18	– .80
Percentage gain or loss[3]	–3	–28	–1	+53	–8	+9	+4	–35	–42

Mean average of water compositions from tuffaceous aquifer (table 3) excluding locations 7, 8, and 15.

[2] Line 1 minus line 3.

[3] Line 4, divided by line 3, times 100.

Oasis Valley is discharged by evapotranspiration is in variance with the findings of Malmberg and Eakin (1962), who estimated that more than 80 percent of the ground water was lost by this process. Malmberg and Eakin based their value on estimates of total areal coverage by phreatophytes, average depth of ground water, and rates of evaporation.

Major variations exist between lines 1 and 3 (table 7) for the other chemical species that cannot be explained by concentration due to evapotranspiration. Silica, fluoride, and potassium show decreases and magnesium and sulfate show large increases. An estimate of the sources and sinks for the concentration excesses and depletions shown in lines 4 and 5 can be made by considering mass-balance relationships.

Based on an initial volume of 1,000 L and assuming a volume-reduction factor of 2.13, 0.80 mole (line 4) or 42 percent (line 5) of the total silica is lost from the ground water in the alluvium. Ground water recharging the alluvium from the tuffaceous aquifer is nearly saturated with respect to silica gel (table 4). The loss of 42 percent of the total silica can thus be explained by silica gel precipitation as silica concentrations are increased in excess of saturation by evapotranspiration. Similarly, 0.18 mole or 35 percent of the dissolved fluoride is lost by fluorite precipitation (fig. 11);

$$Ca^{++} + 2F^- \rightarrow Ca_2F_{2(\text{fluorite})}.$$

A small amount, 0.09 mole, of dissolved calcium is also lost during the formation of fluorite. This amount, when subtracted from a net calcium deficit of 0.01 mole, produces a deficit of 0.10 mole.

The most likely source of excess magnesium (0.08 mole or 64 percent of the total) is from the incongruent dissolution of dolomite.

$$MgCO_{3\,(\text{dolomite})} + H^+ \rightarrow Mg^{++} + HCO_3^-.$$

The excess of magnesium must be balanced by 0.16 mole of excess bicarbonate. This reaction would further increase the bicarbonate deficit to 0.80 mole.

Concentration increases in calcite-saturated ground water (fig. 12) results in calcite precipitation and the loss of bicarbonate;

$$Ca^{++} + HCO_3^- \rightarrow CaCO_{3\,(\text{calcite})} + H^+.$$

However, the loss of 0.80 mole of bicarbonate in the above reaction is not balanced by the loss of only 0.10 mole of calcium. The excess sulfate (0.24 mole or 9 percent) suggests that the dissolution of calcium sulfate,

$$CaSO_{4\,(\text{gypsum})} \rightarrow Ca^{++} + SO_4^=$$

may be a source of both calcium and sulfate.

The net reaction for calcium sulfate dissolution and calcium carbonate precipitation becomes

$$CaSO_{4\,(\text{gypsum})} + HCO_3^- \rightarrow CaCO_{3\,(\text{calcite})} + H^+ + SO_4^=$$

in which calcium is conserved. Net calcium conservation is demonstrated in table 7. The deficit of 0.60 mole of bicarbonate is approximately balanced in the above reaction by an increase of 0.48 mole of sulfate.

SUMMARY AND CONCLUSIONS

The abundance of springs and shallow wells in Oasis Valley provides an excellent opportunity for a detailed geochemical investigation of ground water associated with tuffaceous rocks. These geochemical data, in turn, permit additional insight into the hydrologic features that control the volume and movement of ground water in Oasis Valley.

Most of the dissolved solids, represented principally by sodium, bicarbonate, and silica, are derived from reaction with the tuffaceous rocks. Comparison of these high solute concentrations with reported analyses for intruded crystalline rocks of the same chemical composition suggests that hydrolysis and incongruent dissolution of the volcanic glass phase are the principal reactions between the water and the tuffaceous rock. The relative deficiencies in silica and sodium in hydrated glasses reported by other workers support this conclusion. Bicarbonate is the product of the disassociation of soil-derived carbonic acid by hydrolysis and of ion exchange involving the glass phase. Chloride is also leached preferentially relative to fluoride in the glass phase. The kinetic-reaction rates of tuffaceous rocks appear to be significant in determining chemical concentrations because relative concentrations are at least partially a function of distance and presumably of time spent in movement between recharge and discharge areas.

The ground water infiltrates from the tuffaceous rocks into the valley alluvium through springs and subsurface flow. Direct exchange with the atmosphere as well as transpiration through the vegetation cover occurs as the result of the immediate proximity of the water table to the land surface and soil zone. The resulting decrease in the volume of ground water leads to an increase in chemical concentration. Increases of sodium, chloride, and bicarbonate concentrations plot on the same linear reaction paths as do initial concentration increases attributed to chemical reaction with the tuffaceous rocks. Mass-balance calculations indicate, however, that more than 9 percent of the total sulfate and 53 percent of the magnesium can be attributed to sources outside those in the tuffaceous rocks. Calcium and magnesium concentrations in the ground water are higher in areas to the south and west of Oasis Valley where dolomites and limestones locally crop out. Mass-balance equations indicate that substantial sulfate must be associated with increases in calcium; this relation suggests local dissolution of calcium sulfate minerals either in lacustrine deposits in the valley floor or as hydrothermal alteration products of sulfide minerals.

One of the more interesting geochemical features of Oasis Valley is the aqueous concentration controls exhibited by various mineral phases. Dissolved silica remains constant, corresponding to saturation with respect to amorphous silica. Excess silica produced by chemical reaction and evapotranspiration is removed from the aqueous system as silica gel. Silica gel is observed in fracture fillings at numerous locations in the tuffaceous rocks. Montmorillonite represents the stable clay weathering product formed by Oasis Valley ground water. Although the mineral occurs in the tuffs and alluvium, an aqueous supersaturation of more than two orders of magnitude suggests that formation is slow and montmorillonite does not significantly influence the bulk ground-water composition. Analcime is another common mineral occurring extensively in zeolitized zones within the tuffs. However, undersaturation of an order of magnitude with respect to the aqueous system indicates the zeolitization may occur in localized geochemical environments that are not reflected in the bulk ground-water composition found in Oasis Valley.

With increases in concentration in the alluvium, owing to evapotranspiration, the ground water becomes saturated with calcite, barite, and fluorite. For all three minerals, the aqueous concentration does not exceed saturation even with additional decreases in the volume of ground-water. This situation implies active precipitation of these mineral phases. Approximately 35 percent of the initial fluoride is precipitated in the valley alluvium.

Magnesium initially exhibits large increases in concentration in the alluvial aquifer, but downgradient magnesium reaches a constant concentration that is slightly undersaturated with respect to dolomite. The maximum magnesium concentration seems directly related to the inability of the ground water to dissolve dolomite in excess of the saturation value. The initial amount of potassium is decreased by approximately 28 percent in the valley alluvium; this decrease is probably a result of adsorption and fixation by clay minerals present in the alluvium and soil zones.

Two geochemical contributions can be added to the understanding of the hydrologic processes in Oasis Valley. The geochemical history of the ground water in Oasis Valley seems to be generically related to ground water contained under Pahute Mesa and Gold Flat as suggested by previous workers. Concentrations of three major conservative components, sodium, bicarbonate, and chloride, plot on a well-defined linear trend. Water in the recharge areas of Pahute Mesa and Gold Flat plots in the dilute portion of the trend, and the water of Oasis Valley, representing a more advanced stage in the reaction sequence farther downgradient, plots in the more concentrated part. Secondly, mass balance calculations show that slightly more than half the ground water entering the alluvium in the floor of Oasis Valley is lost as a result of evapotranspiration. This value is considerably lower than had been previously estimated by more indirect methods; consequently, considerably more ground water is discharged by underflow to the Amargosa Desert than had been previously anticipated.

REFERENCES

Benson, L., 1978, Mass transport processes in vitric tuffs of Rainier Mesa, Nevada: Geol. Soc. America Bull. (in press).

Berner, R. A., 1971, Principles of chemical sedimentology: New York, McGraw Hill Book Co., 328 p.

Blankennagel, R. K., and Weir, J. E., Jr., 1973, Geohydrology of the eastern part of Pahute Mesa, Nevada Test Site, Nye County, Nevada: U.S. Geol. Survey Prof. Paper 712–B, p. B1–35.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geol. Survey Tech. Water-Resources Inv., Book 5 Chap. A–1, 160 p.

Budd, S. M., 1961, The mechanisms of chemical reaction between silicate glass and attacking agents—Part 1. Electrophilic and nucleophilic mechanisms of attack: Phys. Chem. Glasses, v. 2, p. 111–114.

Carr, W. J., 1974, Structure and clay alteration, *in* Results of exploration of the Baneberry site, early 1971: U.S. Geol. Survey rept. USGS–474–145, p. 7–18; available *only* from U.S. Dept. Commerce, Natl. Tech. Inf. Service, Springfield, VA 22161.

Carr, W. J., and Quinlivan, W. D., 1966, Geologic map of the Timber Mountain quadrangle, Nevada: U.S. Geol. Survey Quad. Map GQ–503, 1:62,500.

Cornwall, H. R., 1962, Calderas and associated volcanic rocks near Beatty, Nye County, Nevada, *in* Petrologic studies: a volume in honor of A. F. Buddington; A. E. J. Engle, H. L. James, and B. F. Leonard, eds., Geol. Soc. America, p. 357–372.

Cornwall, H. R., and Kleinhampl, F. J., 1961, Geology of Bare Mountain quadrangle, Nevada: U.S. Geol. Survey Quad. Map GQ–157, 1:62,500.

——— 1964, Geology of the Bullfrog quadrangle and ore deposits related to the Bullfrog Hills caldera, Nye County, Nevada and Inyo County, California: U.S. Geol. Survey Prof. Paper 454–J, p. J1–J25.

Davis, S. N., 1964, Silica in streams and ground water: Am. Jour. Sci., v. 262, no. 7, p. 870–891.

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. Geol. Survey Water-Supply Paper 1535–I, p. I1–I170.

Garrels, R. M., and Christ, C. L., 1965, Solutions, minerals and equilibria: New York, Harper and Row, Inc., 450 p.

Garrels, R. M., and Mackenzie, F. T., 1967, Origin of the chemical compositions of some springs and lakes, *in* Equilibrium concepts in natural water systems: Am. Chem. Soc., Advances in Chemistry Series, v. 67, p. 222–242.

Gibbons, A. B., Hinrichs, E. N., and Botinelly, T., 1960, The role of impermeable rocks in controlling zeolitic alteration of tuffs, *in* Geological Survey Research 1960: U. S. Geol. Survey Prof. Paper 400–B, p. B473–475.

Helgeson, H. C., 1969, Thermodynamics of hydrothermal systems at elevated temperatures and pressures: Am. Jour. Sci. v. 367, no. 7, p. 729–804.

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 atmosphere and 0 > to 300 >C: San Francisco, Freeman, Cooper and Co., 254 p

Hem, J. D., 1970. Study and interpretation of the chemical characteristics of natural water: U. S. Geol. Survey Water-Supply Paper 1473, 362 p.

Hemley, J. J., Meyer, C., and Richter, D. H., 1961, Some alteration reactions in the system $Na_2O–Al_2O_3–SiO_2–H_2O$, *in* Geological Survey Research 1961: U.S. Geol. Survey Prof. Paper 424–D, p. D338–D340.

Hoover, D. L., 1968, Genesis of zeolites, Nevada Test Site, *in* Nevada Test Site, Eckel, E. B., ed.: Geol. Soc. America Mem. 110, p. 275–284.

Jones, B. F., 1966, Geochemical evolution of closed basin water in the western Great Basin, *in* Symposium on salt, 2d, v. 1, Geology, geochemistry, mining: Cleveland, Ohio, Northern Ohio Geol. Soc., p. 181–200.

Kittrick, J. A., 1971a, Stability of montmorillonites, I. Belle Fourche and Clay Spur montmorillonites: Soil Sci. America Proc., v. 35, no. 1, p. 140–145.

——— 1971b, Stability of montmorillonites, II, Aberdeen montmorillonite: Soil Sci. America Proc., v. 35, no. 1, p. 820–823.

Lipman, P. W., 1965, Chemical comparison of glassy and crystalline volcanic rocks: U.S. Geol. Survey Bull, 1201–D, 24 p.

Lipman, P. W., Christiansen, R. L., and O'Connor, J. T., 1966, A compositionally zoned ash-flow sheet in southern Nevada: U.S. Geol. Survey Prof. Paper 524–F, 47 p.

Malmberg, G. T., and Eakin, T. E., 1962, Ground-water appraisal of Sarcobatus Flat and Oasis Valley, Nye and Esmeralda Counties, Nevada: Nevada State Engineer, Ground-Water Resources Reconn. Ser. rept. 10, 39 p.

——— 1964, Relation of fluoride content to recharge and movement of ground water in Oasis Valley, southern Nevada, *in* Geological Survey Research 1964: U.S. Geol. Survey Prof. Paper 475–D, p. D189–D191.

Marshall, C. E., 1949, The colloid chemistry of silicate minerals: Agronomy Monograph, v. 1 IX, New York, Academic Press, Inc., 195 p.

Noble, D. C., 1967, Sodium, potassium and ferrous iron contents of some secondary hydrated natural silica glasses: Am. Mineralogist, v. 52, no. 2, p. 280–286.

Noble, D. C., Smith, V. C., and Peck, L. C., 1967, Loss of halogens from crystallized and glassy silicic volcanic rocks: Geochim. et Cosmochim, Acta, v. 31, no. 2, p. 215–223.

O'Connor, J. T., Anderson, R. E., and Lipman, P. W., 1966, Geologic map of the Thirsty Canyon quadrangle, Nevada: U.S. Geol. Survey Quad. Map GQ–524.

Plummer, L. N., and Mackenzie, F. T., 1974, Predicting mineral solubility from rate data: Application to the dissolution of magnesian calcites: Am. Jour. Sci., v. 274, p. 61–83.

Ransome, F. L., Emmons, W. H., and Garrey, G. H., 1910, Geology and ore deposits, Bullfrog District, Nevada: U.S. Geol. Survey Bull. 407, 129 p.

Sheppard, R. A., and Gude, A. J., 1968, Distribution and genesis of authigenic silicate minerals in tuffs of Pleistocene Lake Tecopa, Inyo County, California: U.S. Geol. Survey Prof. Paper 579, 38 p.

——— 1973, Zeolites and associated authigenic silicate minerals in tuffaceous rocks of the Big Sandy Formation, Mohave County, Arizona: U.S. Geol. Survey Prof. Paper 830, 35 p.

Smyshlyaev, S. J., and Edeleva, N. P., 1962, Determination of the solubility of minerals, Solubility product for fluorite: Izv. Vysshikh Vchebn. Zavedenii Khim i Khim. Tekhnologiya, v. 5, p. 871–874.

Truesdell, A. H., 1966, Ion exchange of natural glasses by the electrode method: Am. Mineralogist, v. 51, ncs. 1 and 2, p. 110–122.

Truesdell, A. H., and Jones, B. F., 1974, WATEQ, a computer program for calculating chemical equilibrium of natural waters: Jour. Research, v. 2, no. 2, p. 233–248.

White, D. E., Hem, J. D., and Waring, G. A., 1963, Chemical composition of subsurface waters: U.S. Geol. Survey Prof. Paper 440–F, p. F1–F66.

Winograd, I. J., and Thordarson, William, 1975, Hydrogeologic and hydrochemical framework, south-central Great Basin with special reference to the Nevada Test Site: U.S. Geol. Survey Prof. Paper 712–C, p. C1–C126.

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