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Sources of
Mineral Constituents in
Water from Granitic Rocks
Sierra Nevada
California and Nevada

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1535-I



Sources of Mineral Constituents in Water from Granitic Rocks Sierra Nevada California and Nevada

By J. H. FETH, C. E. ROBERSON, and W. L. POLZER

GEOCHEMISTRY OF WATER

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1535-I

Evaluates mineral-content gains in the snow, snowmelt, ground-water system; considers appropriate thermodynamic equilibria



UNITED STATES DEPARTMENT OF THE INTERIOR

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GEOLOGICAL SURVEY

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CONTENTS

	Page
Abstract.....	I 1
Introduction.....	3
Statement of problem and scope of investigation.....	3
Acknowledgments.....	18
Environment of the springs.....	19
Climate.....	19
Geologic setting.....	20
Regional setting.....	20
Granitic rocks.....	21
Clay minerals.....	22
Local settings of the perennial springs.....	23
Hydrologic setting of the springs.....	30
Chemical implications.....	30
Chemical character of the water and the sources of mineral constituents..	32
Collection of samples and field tests.....	32
Analytical procedures.....	33
Analysis of the data.....	33
General character.....	33
Progressive increases in mineralization.....	35
Concentration by evaporation.....	37
Quartz monzonite and granodiorite groups.....	37
Sources, products, and processes.....	38
Carbon dioxide system.....	39
Silica and cations.....	39
Chloride, sulfate, and nitrate.....	43
Source of anions.....	43
Adsorption of chloride and sulfate.....	44
Seasonal variations of chloride and nitrate.....	46
Relative mobility of common elements and implications as to weather- ing.....	48
Standard procedure.....	49
Release and retention of elements.....	50
Comparisons with water from other sources.....	52
Stream water.....	52
Thermal springs.....	53
Effects of climatic environment on ground water from granitic rocks..	55
Water from volcanic rocks.....	58
Stability relations.....	60
Conclusions.....	66
References cited.....	67

ILLUSTRATIONS

	Page
PLATE 1. Map of parts of California and Nevada showing the Sierra Nevada batholith and sampled springs.....	In pocket
FIGURE 1. Map showing lines of equal runoff in Western States.....	I 17
2. Sketch map showing geology of "Monitor Spring" area.....	25
3. Reconnaissance lithologic map showing environment of three springs in T. 6 N., R. 16 E., Calaveras County, Calif.....	26
4. Geologic sketch profile showing spring area near Calpine....	27
5. Sketch map showing geologic environment of spring in T. 14 N., R. 18 E., Douglas County, Nev.....	28
6. Diagram showing chemical character of springs and of snow..	34
7. Graph showing dissolved solids versus silica and bicarbonate..	36
8. Plot showing bicarbonate versus silica.....	40
9. Plot showing sodium versus silica.....	42
10. Graph showing seasonal variations at "Monitor Spring".....	47
11. Graph showing calculated and measured calcium, thermal springs.....	54
12. Diagram showing chemical character both of water in four environments and of sea water.....	56
13, 14. Stability relations in system:	
13. $K_2O-Al_2O_3-SiO_2-H_2O$	62
14. $Na_2O-Al_2O_3-SiO_2-H_2O$	65

TABLES

	Page
TABLE 1. Chemical analyses of water from granitic terrane in the Sierra Nevada, California and Nevada, and related data..	I 4
2. Concentrations of principal constituents in water from ephemeral and perennial springs.....	16
3. Concentrations of principal mineral constituents in Sierra Nevada snow samples.....	35
4. Changes in average concentration of selected constituents in snow, ephemeral springs, and perennial springs.....	37
5. Comparison of concentrations of major constituents in water from quartz monzonite and granodiorite.....	38
6. Relative mobility of common elements determined from weight-percentage composition of average rock and of average water from springs.....	50
7. Relative mobility of common elements calculated from their concentrations in water from springs and their abundances in rocks, considered by groups.....	51
8. Comparison of mean concentrations of major constituents in ground and surface water.....	53
9. Chemical analyses of water from thermal springs.....	54
10. Concentrations of major constituents in water from springs in volcanic terrane.....	59
11. Standard free energies of formation of compounds and ions at 25° C and 1 atmosphere total pressure.....	60

GEOCHEMISTRY OF WATER

SOURCES OF MINERAL CONSTITUENTS IN WATER FROM GRANITIC ROCKS, SIERRA NEVADA, CALIFORNIA AND NEVADA

By J. H. FETH, C. E. ROBERSON, and W. L. POLZER

ABSTRACT

The natural laboratory provided by the Sierra Nevada allowed study of the problems of how, why, and from what sources ground water acquires mineral content. Understanding of these processes is increasingly significant in a day when industrial and technologic advances require increasing amounts of water meeting certain specifications as to chemical quality. Determination of water quality from a study of the geology of the aquifers and the climatic environment becomes ever more necessary.

The low dissolved-solids content, ranging from 11 to 162 ppm (parts per million), of all the nonthermal water obtained from granitic-rock terrane in the Sierra Nevada allows segregation of some of the processes by which mineral content of the water changes. Starting with snow, the source of virtually all recharge in the region, mineral content increases on the average $7\frac{1}{2}$ times as melt water comes in contact with soil and saprolite, then doubles again during deeper penetration of the water as it moves toward perennial springs. The diversity in chemical type displayed by samples of snow disappears almost instantaneously when the melt water comes in contact with the lithosphere. Water from both perennial springs and ephemeral springs—those sources that yield water only during a short season of melting snow—is uniformly of mixed-cation bicarbonate type.

Silica is overwhelmingly abundant and available, both in the minerals of the region and in their weathering products. Its concentration increases 100 times in the transition from melting snow to water of the ephemeral springs and increases 150 times from snow to perennial springs. Released by hydrolysis of the rock-forming silicate minerals, much of the silica remains at sites of weathering either as part of clay-mineral molecules or as poorly crystallized or amorphous residues. Iron and aluminum are virtually immobile in the environment, as they are retained in products of weathering, probably as hydrous oxides.

The common cations are derived principally by hydrolysis of feldspar, hornblende, and biotite. During early stages of contact between water and the rock, pH is relatively low and the hydrogen-ion content is high. Under these circumstances, potassium and sodium seem to be preferentially released from the mineral lattices. As reaction between hydrogen ions and the minerals continues and total mineral content of the water increases, sodium content tends to level off at about 7 ppm and potassium content tends to level off at about 3 ppm.

Bicarbonate and silica occur in a 1:1 mole ratio until silica content increases to a first limit of about 25 ppm. In a few water samples the 1:1 ratio persists to silica concentrations of about 50 ppm. Initial mole ratios of silica to sodium (2:1) and of silica to bicarbonate (1:1) suggest formation of kaolinite or mont-

morillonite, or both, during weathering of plagioclase feldspar. A 1:1 ratio of silica with respect to sodium, found in some samples, suggests formation of kaolinite by weathering of hornblende. These reactions involve only water and minerals known to be present in the rock and soil of the Sierra Nevada. The spring water is thermodynamically stable with respect to kaolinite.

Carbon dioxide, the source of bicarbonate in the water, comes in small part from melting snow that is in contact with the atmosphere, but it comes mostly from gases contained in the soil. The bicarbonate content in the ephemeral springs is about 7 times that in snow, and in the perennial springs, nearly 20 times that in the snow. The total content of carbon dioxide in the water, calculated from bicarbonate content and pH, is directly correlated with dissolved-solids contents of the water samples.

Sulfate, chloride, and nitrate content of the water is small. Some is brought into the area by the snow, and small increments may be obtained from weathering of the rock-forming minerals. Locally, mineralized water rising in fault zones and mixing with other meteoric water of more shallow circulation adds determinable amounts of sulfate and chloride to water discharged at perennial springs. Most of the nitrate in ground water probably comes from decaying vegetable matter and from the activities of organisms.

There is considerable evidence that chloride and sulfate are removed from solution in some places by adsorption on clay. If this is so, then where conditions of clay content of soil and of pH are suitable to anion sorption (sorption of chloride is effective only where pH is less than about 6.8), chloride cannot confidently be used as a geochemical tracer. Specifically, in this study, the fact that nearly half the ground-water samples had chloride and sulfate contents equivalent to or less than the mean concentrations of those ions in snow made an estimate of the concentration of the water by evaporation impossible, although published meteorologic and hydrologic studies have shown that the evaporation potential in the region is high.

Relative mobility of the common elements was calculated by two methods, both yielding the sequence $Ca \geq Na > Mg > K \geq Si > Fe = Al$, in conformity with the results of most studies by other workers.

Comparison with water from granitic rocks in Idaho, the Mojave Desert, coastal areas in California, and North Carolina shows that the climatic as well as the lithologic environment exercises strong control over water quality. The influence of climate is exerted both by the chemical character of precipitation and its distribution throughout the year and by the effect of climate on the depth and maturity of soil formed. More similarity exists between water from granitic rock and water from volcanic rock in the Sierra Nevada than between water from granitic rock in the Sierra Nevada and water from granitic rock in the Mohave Desert or along the California coast. Water from granite in Idaho and North Carolina is generally comparable with that in the Sierra Nevada. Water from thermal springs in the Sierra Nevada is notably higher in mineral content and in content of sulfate and chloride than is nonthermal water. In the thermal water, as a result of vigorous hydrolysis, pH is commonly 8.0 or higher. Under these conditions, the water is at or near saturation with respect to calcite, and perhaps dolomite, and calcium and magnesium contents are very low.

The geologic environment of the nonthermal springs was studied by mapping in some areas and by laboratory examination of the rocks in thin section and by staining techniques. Quartz monzonite and granodiorite are the most abundant rock types identified. Andesine is the most abundant feldspar. Hornblende and biotite are the only ferromagnesian minerals present in any abundance—biotite is most abundant in the quartz monzonite, hornblende in the granodiorite.

Although, in general, the water samples collected are reasonably assigned to an origin in the granitic rocks, in detail the geologic environments of most of the springs show some complexity. Alluvium and talus are commonly present. At some localities, nearby channels cut in the granitic-rock surface were later filled with volcanic material, commonly well-bedded tuffaceous sediments. Some of the nonthermal springs, and probably all the thermal springs, are associated with faults. In places, dikes of andesite or basalt, or both, occur near spring orifices.

Of the 56 perennial springs sampled, 18 are in quartz monzonite, 18 are in granodiorite, and 20 are in undifferentiated granitic-rock terrane. No statistically significant differences in chemical quality of the water were found among samples from the several groups except that chloride is more concentrated in water from granodiorite. This difference is attributed to the common occurrence of faults in areas where the granodiorite-related springs were found and to admixture of chloride-rich fault-zone water in those places.

The 15 ephemeral-spring localities were not differentiated with respect to granitic-rock type. Water from these sources presumably was in contact only with surficial layers of soil and saprolite for periods ranging from a few hours to a few weeks in contrast to water from perennial springs where residence time is measured in months—possibly years.

INTRODUCTION

STATEMENT OF PROBLEM AND SCOPE OF INVESTIGATION

Where, how, and why water obtains certain substances, especially those from rocks and the products of rock weathering, remains largely an area of uncertainty despite generations of study of the mineralogic and chemical makeup of rocks and of the substances dissolved and entrained in natural water. The present age of diverse and intricate technology, however, requires that we learn the “where,” the “how,” and the “why.” Increasingly, industrial and technologic uses require water that is virtually devoid of certain substances in solution. We must be able to predict where water meeting such specifications may exist naturally or, in a given locality, what pretreatment of the natural water might be required.

This problem of the “where,” the “how,” and the “why” is exceedingly complex. As one of several first steps toward resolving the problem, this report explores a particular and fairly simple aspect—the relation between the chemical character of water issuing from granitic terrane in the Sierra Nevada and the composition of the rocks and their weathering products. Other first steps were covered by Rogers and Feth (1959), Feth and others (1962), and Feth (1962).

Specifically, the conclusions of the present report are derived from chemical analyses of water from (1) 79 samples of snow; (2) 56 non-thermal perennial springs, 8 thermal perennial springs, 15 ephemeral springs or “seeps,” and 34 streams, all in granitic terrane; and (3), for contrast, 25 perennial springs in basaltic or andesitic terrane. The distribution of sampling points is shown on plate 1. The principal chemical analyses of water from granitic terrane are given in table 1.

TABLE 1.—*Chemical analyses of water from granitic terrane*

[Data in parts per million]

Labo- ratory No.	Location	Date of col- lection	Tem- pera- ture (de- grees F)	Sil- ica (SiO ₂)	Alu- mi- num (Al)	Iron (Fe)	Cal- cium (Ca)	Mag- ne- sium (Mg)	Stron- tium (Sr)	Sodi- um (Na)	Po- tas- sium (K)
EPHEMERAL SPRINGS											
748--	NW $\frac{1}{4}$ sec. 15, T. 17 N., R. 15 E., Nevada County, Calif.	5-27-58	58	26	0.00	0.00	5.6	1.9	-----	3.9	1.2
750--	NE $\frac{1}{4}$ sec. 21, T. 17 N., R. 14 E., Nevada County, Calif.	-----do-----	-----	3.3	.00	.00	.8	.0	-----	2.6	.4
1132--	NE $\frac{1}{4}$ sec. 6, T. 14 N., R. 19 E., Douglas County, Nev.	10-19-59	40	28	.00	.01	5.6	2.9	-----	4.6	2.5
1218--	NW $\frac{1}{4}$ sec. 24, T. 11 N., R. 16 E., El Dorado County, Calif.	5-2-60	57	24	.04	.02	4.4	.7	-----	4.2	1.2
1222--	NE $\frac{1}{4}$ sec. 31, T. 12 N., R. 18 E., El Dorado County, Calif.	5-3-60	38	13	.12	.07	1.6	.5	-----	2.4	1.5
1226--	SW $\frac{1}{4}$ sec. 32, T. 15 N., R. 19 E., Ormsby County, Nev.	5-4-60	51	37	.04	.01	4.9	1.1	-----	6.3	2.1
1232--	NW $\frac{1}{4}$ sec. 15, T. 17 N., R. 15 E., Nevada County, Calif.	5-5-60	53	5.2	.00	.01	1.0	.1	-----	1.2	.2
1233--	NW $\frac{1}{4}$ sec. 15, T. 17 N., R. 15 E., Nevada County, Calif., adjacent to sample 1232 but having deeper penetration into the rock.	-----do-----	47	17	.08	.04	2.6	.9	-----	2.6	.8
1256--	NE $\frac{1}{4}$ sec. 13, T. 8 N., R. 19 E., Alpine County, Calif.	6-3-60	47	15	.02	.02	3.1	.9	-----	1.9	.7
1499--	NW $\frac{1}{4}$ sec. 30, T. 17 N., R. 19 E., Washoe County, Nev.	5-30-61	-----	10	-----	-----	3.4	.0	-----	2.9	1.8
1500--	-----do-----	-----do-----	43	11	-----	-----	2.2	.0	-----	2.9	2.1
1502--	-----do-----	-----do-----	-----	13	-----	-----	1.8	.6	-----	2.3	.3
1504--	NW $\frac{1}{4}$ sec. 30, T. 17 N., R. 19 E., Washoe County, Nev.	-----do-----	44	13	-----	-----	1.4	.2	-----	2.5	.3
1506--	NW $\frac{1}{4}$ sec. 12, T. 11 N., R. 17 E., El Dorado County, Calif.	5-31-61	-----	8.1	-----	-----	1.3	.4	-----	1.3	.3
1531--	NW $\frac{1}{4}$ sec. 22, T. 6 N., R. 19 E., Tuolumne County, Calif.	8-22-61	62	23	.00	.12	7.0	.3	0.12	3.9	1.0

in the Sierra Nevada, California and Nevada, and related data
 except as indicated]

Bicarbonate (HCO ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved Solids (calculated)	Specific Conductance (micro-mhos at 25° C)	pH		Remarks	Clay minerals ¹
Laboratory	Field							Laboratory	Field		
EPHEMERAL SPRINGS—Continued											
38	-----	2.4	0.00	0.0	0.0	60	64	7.1	-----	Snowmelt passing through joints in granite. Altitude 6,100 ft.	
6.0	-----	0	.9	.0	.1	11	16	6.4	-----	Snowmelt passing through saprolite and soil. Altitude 6,500 ft.	
41	-----	2.0	.1	.1	.0	66	67	7.5	-----	Trickle from brecciated quartz monzonite. Altitude 6,900 ft.	
31	30	.2	.1	.1	.02	50	47	7.4	7.5	Water dripping from rock ledge after flow over and through weathered rock. Altitude 6,000 ft.	
12	-----	3.6	.5	.1	.0	29	28	5.7	5.6	Water seeping through soil into dug hole 10 ft. from melting snowbank. Altitude 6,500 ft.	
42	37	.6	.2	.2	.0	73	68	6.9	8.2	Trickle from brecciated and weathered quartz monzonite. Altitude 6,600 ft.	
5	5	1.6	.3	.0	.0	12	8	6.1	6.3	Discharge <1 gpm from soil overlying granite rock. Altitude 6,800 ft.	
20	19	.9	.2	.1	.00	35	35	5.8	5.9	-----do-----	
19	21	.7	.1	.0	.0	32	31	6.2	6.3	Discharge 1 gpm from weathered rock and boulders. Altitude 7,600 ft.	
14	-----	.0	2.0	-----	-----	27	30	5.5	-----	Water bailed from auger hole 3 ft deep in bare soil. Sample deep brown. Altitude 8,800 ft.	
11	14	3.0	1.8	-----	-----	28	29	5.3	5.8	Natural discharge from soil in zone of vegetation near auger hole (above). Sample light brown.	
12	-----	.0	.1	-----	-----	24	19	6.4	-----	Discharge 5 gpm from hillside about 50 yd below site of sample 1500. Sample clear.	
9	-----	.0	.6	-----	-----	22	17	5.7	6.2	Discharge 3 gpm from soil and saprolite into stream channel about 100 yd below auger hole (analysis 1490). Sample muddy.	
7	-----	.0	.2	-----	-----	15	12	5.6	6.2	Discharge 1 gpm from soil and saprolite on wall of highway borrow pit. Sample charged with white clay (gibbsite). Altitude 7,000 ft.	
34	32	0	.4	.0	.1	53	56	6.8	6.9	Discharge <1 gpm from soil in meadow. Thick growth of alders. Altitude 5,600 ft.	

See footnote at end of table.

TABLE 1.—Chemical analyses of water from granitic terrane in the

Labo- ra- tory No.	Location	Date of col- lection	Tem- pera- ture (de- grees F)	Sil- ica (SiO ₂)	Alu- mi- num (Al)	Iron (Fe)	Cal- cium (Ca)	Mag- ne- sium (Mg)	Stron- tium (Sr)	Sod- ium (Na)	Po- tas- sium (K)
PERENNIAL SPRINGS Quartz monzonite group											
1127..	At head of South Fork, Crooked Creek, Bucks Peak, approximately in sec. 28, T. 5 S., R. 35 E. (unsurveyed), Mono County, Calif.	10-17-59	45	20	0.00	0.06	16	3.6	-----	7.7	1.0
1138..	About 3¼ miles west of Woodfords, NE¼ sec. 31, T. 11 N., R. 19 E., Alpine County, Calif.	10-21-59	47	23	.02	.00	11	1.7	-----	4.9	1.2
1153..	Harry Birch Spring about 9 miles northwest of Independence, NW¼ sec. 17, T. 12 S., R. 34 E., Inyo County, Calif.	11- 9-59	58	18	.00	.01	26	2.4	-----	7.4	1.5
1217..	Three miles east of Kyburz, SW¼ sec. 20, T. 11 N., R. 16 E., Amador County, Calif.	5- 2-60	-----	35	.02	.03	12	2.3	-----	6.7	1.9
1250..	About 6 miles northwest of Carson City, SE¼ sec. 21, T. 16 N., R. 19 E., Washoe County, Nev.	6- 2-60	52	22	.02	.07	15	1.9	-----	7.0	2.1
1255..	About 2 miles west of Ebbetts Summit, NW¼ sec. 13, T. 8 N., R. 19 E., Alpine County, Calif.	---do---	50	20	.02	.02	2.2	.5	-----	2.1	1.1
1257..	About 3 miles west of Ebbetts Summit, SE¼ sec. 16, T. 8 N., R. 19 E., Alpine County, Calif.	6- 3-60	49	11	.04	.00	1.6	.5	-----	1.8	.4
1131..	"Monitor Spring," about 7¼ miles southwest of Carson City, SE¼ sec. 32, T. 15 N., R. 19 E., Ormsby County, Nev.	10-19-59	50	23	.00	.02	11	4.9	-----	5.4	2.6
1158..	do	11-10-59	50	-----	-----	-----	11	3.3	-----	-----	-----
1224..	do	5- 4-60	47	24	.02	.02	11	2.8	-----	5.3	2.4
1330..	do	9-20-60	51	24	.00	.00	11	3.5	0.12	5.4	2.4
1480..	do	4-21-61	24	-----	-----	-----	12	2.4	-----	5.5	2.5
1524..	do	7-20-61	24	.00	.00	.02	12	2.5	.10	5.2	2.5
1568..	do	9-30-61	50	25	.00	.02	11	2.9	.13	5.8	2.8
1519..	Iron Spring 1¼ miles east of Yosemite Village, approximately in SE¼ sec. 22, T. 2 S., R. 22 E. (unsurveyed), Tuolumne County, Calif.	7-17-61	50	14	.00	.17	4.8	.0	.06	1.5	1.1

Sierra Nevada, California and Nevada, and related data—Continued

Bicarbonate (HOC ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved Solids (calculated)	Specific Conductance (micro-mhos at 25° C)	pH		Remarks	Clay minerals ¹
Laboratory	Field							Laboratory	Field		
PERENNIAL SPRINGS—Continued											
Quartz monzonite group—Continued											
66	-----	12	1.0	0.1	0.00	94	134	7.4	-----	Discharge <1 gpm from small cave in granite boulders. Altitude 10,000 ft.	
55	-----	2.5	.2	.1	.1	72	93	6.9	-----	Discharge 7-10 gpm from masonry collector. Quartz monzonite terrane. Altitude 6,800 ft.	
94	-----	14	1.2	.6	.8	118	189	7.9	-----	Discharges from quartz monzonite talus and soil. Altitude 4,900 ft.	
69	68	2.4	1.0	.0	.0	95	110	6.3	6.2	Discharges from masonry collector. Alaskite terrane, deeply weathered. Spring destroyed by highway construction, 1961. Altitude 3,700 ft.	1>>>3
76	80	1.1	.3	.0	.1	87	120	7.6	7.9	Discharges 5 gpm from aplitic quartz monzonite talus. Altitude 5,500 ft.	
17	19	.7	.1	.1	.0	35	28	6.2	6.2	Discharge 1 gpm from several orifices in deeply weathered quartz monzonite. Sample from discharge channel below all orifices. Altitude 8,100 ft.	2>3>>1
10	13	.9	.1	.0	.0	21	18	6.6	6.9	Discharge 3-5 gpm from quartz monzonite. Altitude 7,600 ft.	
67	-----	1.8	.4	.0	.5	83	110	7.1	-----	Discharge 2 gpm from joints in quartz monzonite (Fig. 2). Altitude 6,300 ft.	2>>>1>3 (In each of 5 samples taken at 1-ft intervals across shear zone adjacent to spring.)
67	-----	-----	-----	-----	-----	-----	-----	6.7	-----	Discharge 2 gpm.	
66	64	3.1	.7	.1	.0	82	106	7.1	7.0	Discharge 1 gpm.	
67	71	3.2	.4	.1	.4	84	109	7.2	7.1	do.	
66	72	0	.8	.0	.1	80	106	7.0	7.3	Discharge not measured.	
66	-----	.2	.5	.1	.3	80	108	6.9	-----	Discharge 1½ gpm.	
68	70	.0	.4	.1	.4	82	108	7.39	7.1	Discharge 1 gpm.	
16	-----	.2	3.2	.1	.2	33	38	6.0	-----	Discharge 5-10 gpm from morainal debris, mostly of quartz monzonite. Altitude 4,000 ft.	4

See footnote at end of table.

TABLE 1.—Chemical analyses of water from granitic terrane in the

Laboratory No.	Location	Date of collection	Temperature (degrees F)	Silica (SiO ₂)	Aluminum (Al)	Iron (Fe)	Calcium (Ca)	Magnesium (Mg)	Strontium (Sr)	Sodium (Na)	Potassium (K)
PERENNIAL SPRINGS—Continued											
Quartz monzonite group—Continued											
1520..	Fern Spring 2½ miles west of Yosemite Village, approximately in SW¼ sec. 32, T. 2 S., R. 21 E. (unsurveyed) Tuolumne County, Calif.	7-18-61	46	15	0.00	0.00	4.4	0.0	0.03	1.7	0.7
1529..	Adjacent to Cow Creek, SE¼ sec. 32, T. 5 N., R. 18 E., Tuolumne County, Calif.	8-22-61	53	57	.06	.19	14	3.8	.30	7.0	2.5
1559..	In Feather River Canyon, NW¼ sec. 31, T. 24 N., R. 6 E., Plumas County, Calif.	9-25-61	54	27	.00	.01	5.9	1.0	.12	5.4	1.8
1561..	About 1½ miles north of Calpine, NE¼ sec. 18, T. 21 N., R. 14 E., Sierra County, Calif.	9-26-61	56	51	.03	.02	20	4.2	.31	13	2.4
1565..	At Big Bend Forest Camp, NE¼ sec. 28, T. 17 N., R. 13 E., Nevada County, Calif.	9-27-61	44	26	.02	.02	5.6	.5	.03	4.4	1.1
1569..	About ¼ mile southeast of Meyers, NE¼ sec. 32, T. 12 N., R. 18 E., El Dorado County, Calif.	10-17-61	41	29	.03	.00	7.0	.6	.08	5.5	1.6
1571..	About ½ mile south of Meyers, north of center of sec. 32, T. 12 N., R. 18 E., El Dorado County, Calif.	---do---	48	24	.00	.00	12	.8	.05	6.4	2.3
1577..	At Westfall Ranger Station, SW¼ sec. 35, T. 5 S., R. 21 E., Madera County, Calif.	10-24-61	48	24	.00	.00	2.6	.0	.04	3.8	.6
1580..	Near Shaver Lake Point, NW¼ sec. 13, T. 9 S., R. 24 E., Fresno County, Calif.	10-25-61	54	31	.00	.00	4.6	.0	.06	5.6	1.4
PERENNIAL SPRINGS											
Granodiorite group											
1170..	About 2 miles south of Meyers, NW¼ sec. 5, T. 11 N., R. 18 E., El Dorado County, Calif.	12-11-59	48	27	.01	.00	8.8	.6	-----	15	2.3
1172..	Stambaugh Spring 1½ miles north of Zephyr Cove, SW¼ sec. 34, T. 14 N., R. 18 E., Douglas County, Nev.	12-12-59	47	20	.02	.00	16	6.3	-----	7.0	2.5
1572..	---do---	10-17-61	48	20	.02	.01	21	3.3	.11	7.1	3.1

Sierra Nevada, California and Nevada, and related data—Continued

Bicarbonate (HOC ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved Solids (calculated)	Specific Conductance (microhos at 25° C)	pH		Remarks	Clay minerals ¹
Laboratory	Field							Laboratory	Field		
PERENNIAL SPRINGS—Continued Quartz monzonite group—Continued											
21	30	0.4	0.3	0.0	0.2	33	36	6.3	-----	Discharge 15 gpm from alluvium at base of granitic cliff. Altitude 3,900 ft.	
84	95	.4	.4	.1	.1	127	131	7.4	7.45	Discharge 1½ gpm from quartz monzonite boulders and soil. Altitude 5,000 ft.	
33	35	5.2	1.8	.1	.0	65	69	6.57	6.8	Discharge 2 gpm from pipe set in quartz monzonite boulders and soil. Altitude 1,760 ft.	4
109	93	4.6	.9	.1	.2	150	143	7.12	7.55	Discharge <1 gpm from hole dug into deeply weathered quartz monzonite; allowed to flow 10 minutes before sampling. Altitude 5,200 ft. See figure 4.	4
31	34	.9	.1	.1	.1	54	52	6.24	6.5	Discharge 1-2 gpm from quartz monzonite talus. Older gravel containing granitic and volcanic-rock clasts at orifice level nearby. Altitude 6,000 ft.	4
40	41	.0	.2	.0	.1	64	65	6.3	6.7	Discharge 3-5 gpm from alluvium derived from quartz microcline gneiss. Thick growth of alders. Altitude 6,600 ft.	4
63	63	1.6	.3	.1	.1	79	102	7.4	7.5	Discharge 8½ gpm from concrete collector. Alluvial basin in quartz monzonite terrane. Altitude 6,500 ft.	4
18	18	.0	.5	.0	.2	41	33	5.8	6.08	Discharge 2 gpm from concrete collector, quartz microcline gneiss and alluvium surrounding. Altitude 5,000 ft.	
28	30	.0	.7	.1	.1	57	51	5.8	6.00	Discharge <1 gpm from hose at storage tank, quartz monzonite surrounding.	
PERENNIAL SPRINGS—Continued Granodiorite group											
55	-----	9.9	6.0	.2	.0	97	121	7.1	-----	Discharge 1-2 gpm from alluvium in quartz diorite terrane. Altitude 6,400 ft.	
105	-----	1.2	.5	.1	.1	106	163	6.8	-----	Discharge 50 gpm at overflow pipe from metal reservoir. Granodiorite and lake deposits in area (fig. 5). Altitude 6,300 ft.	
103	108	.0	.4	.0	.1	106	164	7.4	7.7	Discharge 30 gpm.	

See footnote at end of table.

TABLE 1.—*Chemical analyses of water from granitic terrane in the*

Laboratory No.	Location	Date of collection	Temperature (degrees F)	Silica (SiO ₂)	Aluminum (Al)	Iron (Fe)	Calcium (Ca)	Magnesium (Mg)	Strontium (Sr)	Sodium (Na)	Potassium (K)
PERENNIAL SPRINGS—Continued											
Granodiorite group—Continued											
1286..	About ¼ mile north of General Sherman Tree, Sequoia National Park, SW¼ sec. 29, T. 15 S., R. 30 E., Tulare County, Calif.	8-9-60	53	24	0.02	0.13	3.6	0.5	-----	3.2	1.0
1287..	About ¼ mile north of Little Baldy Saddle, Sequoia National Park, NW¼ sec. 14, T. 15 S., R. 29 E., Tulare County, Calif.	---do---	56	11	.01	.02	1.2	.2	-----	2.1	.6
1293..	About 2¼ miles north of California Hot Springs, NE¼ sec. 19, T. 23 S., R. 31 E., Tulare County, Calif.	8-11-60	53	39	.02	.00	24	5.7	-----	11	2.1
1294..	Chute Spring 3 miles north of California Hot Springs, NE¼ sec. 20, T. 23 S., R. 31 E., Tulare County, Calif.	---do---	-----	43	.03	.03	15	4.4	-----	10	2.6
1295..	At Holey Meadow Campground, SW¼ sec. 3, T. 23 S., R. 31 E., Tulare County, Calif.	---do---	50	28	.01	.00	4.1	.7	-----	3.8	.6
1296..	At Long Meadow Campground, NW¼ sec. 36, T. 22 S., R. 31 E., Tulare County, Calif.	---do---	52	46	.00	.01	7.2	.4	-----	9.8	.9
1521..	Black Spring 2¼ miles west of Yosemite Village, approximately in NW¼ sec. 34, T. 2 S., R. 21 E. (unsurveyed), Mariposa County, Calif.	7-18-61	50	21	.00	.00	9.6	1.2	0.05	3.4	1.8
1522..	At Yosemite Creek on Tioga Pass Road, SE¼ sec. 17, T. 1 S., R. 22 E., Mariposa County, Calif.	---do---	-----	8.8	.00	.00	1.0	.0	.01	.8	.2
1530..	About 15 miles by road northeast of Strawberry, NW¼ sec. 32, T. 6 N., R. 19 E., Tuolumne County, Calif.	8-22-61	51	17	.00	.00	2.4	.2	.04	2.3	.3
1539..	Beside Tioga Pass Road 2¼ miles from floor of Yosemite Valley, SW¼ sec. 25, T. 2 S., R. 20 E., Mariposa County, Calif.	9-13-61	50	27	.00	.00	5.4	.5	.06	5.3	1.4
1566..	At Hampshire Rock Campground, NE¼ sec. 27, T. 17 N., R. 13 E., Placer County, Calif.	9-27-61	50	16	.03	.03	11	.6	.06	8.9	1.8
1567..	Cold Spring at Cold Spring Campground, NE¼ sec. 25, T. 17 N., R. 13 E., Nevada County, Calif.	---do---	44	13	.02	.00	4.3	.2	.04	9.1	1.0

Sierra Nevada, California and Nevada, and related data—Continued

Bicarbonate (HOC ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved Solids (calculated)	Specific Conductance (micro-mhos at 25° C)	pH		Remarks	Clay minerals ¹
Laboratory	Field							Laboratory	Field		
PERENNIAL SPRINGS—Continued											
Granodiorite group—Continued											
19	18	1.7	0.7	0.1	0.0	44	35	7.0	9.1	Discharge 1½ gpm from pipe. Source in quartz diorite and alluvium. Altitude 6,800 ft.	2>1>3
9	10	2.3	.8	.0	.0	23	16	5.9	5.9	Discharge 2 gpm from rubble and soil derived from granodiorite. Altitude 7,200 ft.	4
120	119	6.6	6.0	.1	.5	154	211	6.9	6.4	Discharge 1 gpm from rubble and soil derived from granodiorite. Pollution by livestock possible. Altitude 4,300 ft.	1>3
83	84	5.3	5.0	.1	1.2	128	162	6.8	6.3	Discharge 1 gpm from pipe; spring orifice boxed in. In alluvium; quartz diorite nearby. Altitude 4,600 ft.	
26	24	3.3	.6	.0	.0	54	43	6.1	5.5	Discharge 1 gpm from masonry collector; granodiorite terrane. Altitude 6,400 ft.	4
48	46	2.1	1.2	.1	.0	91	83	6.2	5.5	Discharge from concrete collector; unmeasurable. Granodiorite terrane. Altitude 6,000 ft.	4
46	56	2.4	.3	.1	.1	63	78	7.1	-----	Discharge 2-5 gpm from beneath tree roots in alluvium derived from quartz diorite. Altitude 3,900 ft.	3>1=4
8	16	.2	.0	.0	.0	15	11	6.8	-----	Discharge <1 gpm from alluvium and granodiorite boulders; flows over bare-rock joint surface. Altitude 7,500 ft.	4
14	14	.0	.2	.0	.0	29	25	5.6	5.8	Discharge <1 gpm from joints in fresh granodiorite. Tuff-filled channel 5 ft down gradient from orifice. Altitude 6,400 ft.	4 (? 1, 3)
36	40	1.6	.5	.1	.0	60	57	7.49	6.74	Discharge <1 gpm from rubble and soil derived from granodiorite. Altitude 5,200 ft.	
59	64	3.3	.5	.1	.1	71	102	7.71	7.6	Discharge 1 gpm from concrete collector in alluvium. Ledges of granodiorite 30-50 ft upgradient. Altitude 5,800 ft.	4
19	21	5.5	10	.1	.6	53	76	5.79	6.2	Discharge 6 gpm from pipe set in boulders of granodiorite. Pollution from campground waste possible. Altitude 6,000 ft.	4 (? 1, 3)

See footnote at end of table.

TABLE 1.—Chemical analyses of water from granitic terrane in the

Labo- ratory No.	Location	Date of col- lection	Tem- pera- ture (de- grees F)	Sil- ica (SiO ₂)	Alu- min- um (Al)	Iron (Fe)	Cal- cium (Ca)	Mag- ne- sium (Mg)	Stron- tium (Sr)	Sodi- um (Na)	Po- tas- sium (K)	
PERENNIAL SPRINGS—Continued												
Granodiorite group—Continued												
1573..	About 1½ miles north of Emerald Bay State Park, NW¼ sec. 28, T. 13 N., R. 17 E., El Dorado County, Calif.	10-18-61	44	15	0.03	0.01	2.8	0.1	0.04	2.2	1.4	
1574..	At Emerald Bay Summer Homes Tract, NE¼ sec. 21, T. 13 N., R. 17 E., El Dorado County, Calif.	---do---	44	23	.02	.03	6.5	.8	.08	3.9	1.7	
1579..	Alder Spring at Alder Springs, NW¼ sec. 18, T. 10 S., R. 24 E., Fresno County, Calif.	10-25-61	50	39	.00	.00	6.3	.5	.08	8.2	1.1	
1581..	About 37 miles by road east of Fresno, NE¼ sec. 32, T. 13 S., R. 26 E., Fresno County, Calif.	10-26-61	70	53	.00	.00	21	4.1	.15	14	4.5	
PERENNIAL SPRINGS—Continued												
Granitic rocks, undifferentiated												
811...	About 6½ miles west of Sonora Pass, approxi- mately in sec. 31, T. 6 N., R. 21 E., Alpine County, Calif.	8-29-58	-----	26	.05	.00	18	1.5	-----	4.9	3.0	
1147..	In Little Round Valley, approximately in sec. 36, T. 4 S., R. 29 E., Mono County, Calif.	11- 8-59		50	19	.01	.03	9.2	.7	-----	6.9	.6
1148..	At Sky Meadow Ranch, NW¼ sec. 14, T. 5 S., R. 30 E., Mono County, Calif.	---do---		47	20	.00	.01	6.1	.9	-----	6.8	.1
1149..	Near Paradise Camp, NE¼ sec. 26, T. 5 S., R. 30 E., Mono County, Calif.	---do---	Cold	16	.00	.00	10	1.2	-----	6.2	.8	
1171..	Folsom Spring 1 mile north of Stateline, SW¼ sec. 23, T. 13 N., R. 13 E., Douglas County, Nev.	12-12-59		47	21	.00	.17	16	2.3	-----	8.2	2.2
1245..	Tragedy Spring, SW¼ sec. 7, T. 9 N., R. 17 E., El Dorado County, Calif.	5-31-60		40	32	.00	.00	4.4	1.1	-----	1.8	1.4
1246..	About 4 miles west of Minden, SE¼ sec. 33, T. 13 N., R. 19 E., Douglas County, Nev.	6- 1-60		64	19	.03	.05	20	2.0	-----	7.1	3.0
1247..	About 100 yds west from sample 1246.	---do---		55	15	.02	.00	14	1.0	-----	6.0	2.0
1248..	About 5 miles southwest of Minden, SW¼ sec. 9, T. 12 N., R. 19 E., Douglas County, Nev.	---do---		52	14	.02	.04	7.9	.3	-----	4.8	.6

Sierra Nevada, California and Nevada, and related data—Continued

Bicarbonate (HOC ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved Solids (calculated)	Specific Conductance (micro-mhos at 25° C)	pH		Remarks	Clay minerals ¹
Laboratory	Field							Laboratory	Field		
PERENNIAL SPRINGS—Continued											
Granodiorite group—Continued											
13	15	1.6	0.2	0.1	2.2	32	31	6.5	7.3	Discharge <1 gpm from hole dug in deeply weathered and sheared granodiorite. Allowed to flow 5 min. before sampling. Altitude 6,800 ft.	4 (? 2, 3)
37	38	.0	.2	.1	.1	54	59	6.8	7.25	Discharge 5 gpm from boulders and soil at base of mountain of granodiorite. Altitude 7,000 ft.	4 (? 2)
42	45	.0	1.7	.1	.1	78	75	5.9	6.09	Discharge <1 gpm from orifice in granodiorite in spring house. Altitude 4,500 ft.	
119	113	1.2	3.0	.1	3.0	162	210	6.8	7.09	Discharge <1 gpm from roadside drinking fountain. Granodiorite terrane. Altitude 1,600 ft.	
PERENNIAL SPRINGS—Continued											
Granitic rocks, undifferentiated—Continued											
82	-----	.5	.2	.1	.0	95	133	7.6	-----	Discharge not recorded. No rock sample taken. Altitude 8,000 ft.	
45	-----	3.3	.3	.2	.9	63	85	7.6	-----	Discharge not recorded. No rock sample taken. Altitude 7,200 ft.	
34	-----	3.2	.2	.1	.2	55	66	6.5	-----	Discharge 50 gpm from granitic rubble and soil. Orifice area inaccessible. Altitude 7,200 ft.	
48	-----	3.4	.2	.1	1.0	63	87	6.7	-----	Discharge 30 gpm from dense thicket of shrubs and trees. Granitic rubble and soil surrounding. Altitude 5,900 ft.	
84	-----	3.3	.7	.1	.3	96	135	7.3	-----	Discharge 5 gpm from alluvium below highway grade. Terrane probably granodiorite. Altitude 6,300 ft.	3 > 4
23	26	1.2	.2	.0	.6	54	41	6.2	6.8	Discharge 15-25 gpm; orifice not found. Granitic rocks nearby; volcanic rocks cap surrounding ridges. Altitude 7,900 ft.	
93	96	.8	.5	.1	.0	98	147	7.7	7.9	Discharge 15-25 gpm from alluvium in granitic terrane. Orifice inaccessible. Altitude 5,100 ft.	
67	68	.5	.8	.0	.0	72	108	7.7	7.5	Discharge 10 gpm from granitic rubble and soil; orifice concealed. Altitude 5,100 ft.	
35	38	2.7	.3	.3	1.1	49	65	6.8	7.4	Discharge 3 gpm from alluvium in area of granitic rocks. Altitude 5,100 ft.	4 (? 2, 3)

See footnote at end of table.

TABLE 1.—*Chemical analyses of water from granitic terrane in the*

Laboratory No.	Location	Date of collection	Temperature (degrees F)	Silica (SiO ₂)	Aluminum (Al)	Iron (Fe)	Calcium (Ca)	Magnesium (Mg)	Strontium (Sr)	Sodium (Na)	Potassium (K)
PERENNIAL SPRINGS—Continued											
Granitic rocks, undifferentiated—Continued											
1249..	About 7 miles northwest of Carson City, NE $\frac{1}{4}$ sec. 21, T. 16 N., R. 19 E., Washoe County, Nev.	6- 2-60	53	24	0.02	0.02	14	1.7	-----	7.9	1.7
1251..	About 5 miles west of Minden, NE $\frac{1}{4}$ sec. 4, T. 12 N., R. 19 E., Douglas County, Nev.	---do---	61	17	.03	.30	14	2.1	-----	7.7	1.3
1252..	Closely adjacent to sample 1251.	---do---	69	19	.04	.01	16	3.9	-----	7.6	1.7
1259..	Black Spring about 4 miles southwest of Big Meadow, NE $\frac{1}{4}$ sec. 15, T. 6 N., R. 16 E., Calaveras County, Calif.	6- 3-60	41	13	.02	.01	1.6	.5	-----	1.5	.4
1534..	---do---	8-23-61	52	14	.00	.10	2.2	.2	0 05	1.5	.5
1535..	Poison Spring about 3 miles southwest of Big Meadow, NW $\frac{1}{4}$ sec. 11, T. 6 N., R. 16 E., Calaveras County, Calif.	---do---	44	17	.00	.03	3.9	.2	.06	2.0	.5
1331..	At Spooner Summit, SW $\frac{1}{4}$ sec. 6, T. 14 N., R. 19 E., Douglas County, Nev.	9-20-60	49	16	.00	.01	18	6.1	.24	5.2	1.4
1532..	Cottage Spring about 5 miles east of Dorrington, NE $\frac{1}{4}$ sec. 23, T. 6 N., R. 16 E., Calaveras County, Calif.	8-23-61	51	54	.00	.02	15	5.5	.29	5.7	4.4
1541..	About 7 $\frac{1}{2}$ miles west of Sonora Pass, approximately sec. 34, T. 6 N., R. 20 E. (unsurveyed), Tuolumne County, Calif.	9-14-61	50	25	.19	.02	18	3.2	.26	5.0	3.0
1542..	At Dardenelle, NE $\frac{1}{4}$ sec. 25, T. 6 N., R. 19 E., Tuolumne County, Calif.	---do---	45	24	.04	.14	20	2.5	.24	5.3	2.0
1543..	At Brightman Flat Ranger Station near Dardenelle, approximately in SW $\frac{1}{4}$ sec. 24, T. 6 N., R. 19 E., (unsurveyed), Tuolumne County, Calif.	---do---	45	20	.02	.01	17	1.8	.19	7.2	1.0
1544..	At Eureka Valley Campground, 2 miles east of Dardenelle, NW $\frac{1}{4}$ sec. 23, T. 6 N., R. 20 E., Tuolumne County, Calif.	---do---	62	27	.02	.00	14	2.5	.22	8.0	2.1

Sierra Nevada, California and Nevada, and related data—Continued

Bicarbonate (HOC ₃)		Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO ₃)	Dissolved Solids (calculated)	Specific Conductance (microhmhos at 25° C)	pH		Remarks	Clay minerals ¹
Laboratory	Field							Laboratory	Field		
PERENNIAL SPRINGS—Continued											
Granitic rocks, undifferentiated—Continued											
75	78	1.2	0.5	0.0	0.0	88	120	7.3	7.7	Discharge 5 gpm from alluvium in granitic terrane. Orifice inaccessible. Altitude 5,100 ft.	
70	72	1.0	.6	.1	.3	79	114	6.9	7.3	Discharge 1-2 gpm from channel in alluvium; granitic terrane. Altitude 5,000 ft.	
88	89	1.0	.2	.2	.0	93	138	7.4	7.4	Discharge 3 gpm in alluvial channel; granitic terrane. Altitude 5,200 ft.	
10	14	.5	.4	.0	.0	23	20	5.7	5.6	Discharge 10-15 gpm from alluvial basin. Clasts include quartz monzonite and volcanic rocks. Volcanic rocks cap quartz monzonite hills surrounding. Altitude 6,400 ft. See figure 3.	4 (? 1, 3)
12	14	.0	.2	.0	.0	25	22	5.4	5.75		4
17	20	.0	.3	.0	.0	32	31	5.6	5.75	Discharge 3-5 gpm from alluvial basin. More volcanic rock in vicinity than near No. 1259. Altitude 6,600 ft. See figure 3.	(? 1, 3) 4
105	107	1.0	.3	.1	.3	100	164	7.4	7.2	Discharge <1 gpm from concrete collector in alluvium. Spring dry when revisited 1961. Altitude 7,200 ft.	
97	100	.0	.3	.0	.1	133	152	7.0	6.9	Discharge 1-2 gpm from pipe. Collector in alluvium. Granitic rock and bedded tuff in area. Volcanic clasts in alluvium. Altitude 5,600 ft.	4
88	90	2.2	.5	.1	.0	101	138	7.57	7.90	Discharge 2 gpm from pipe. Orifice in soil derived from granitic rock. Altitude 7,000 ft.	
91	92	1.6	.3	.1	.4	101	142	6.60	6.65	Discharge <1 gpm. Orifice in granitic boulders and soil. No rock sample. Altitude 6,000 ft.	
73	76	5.2	2.0	.1	.0	90	129	6.65	6.60	Discharge not recorded. No rock sample. Altitude 6,200 ft.	
80	91	2.2	.3	.1	.0	96	124	7.58	7.92	Sample from campground water faucet. Orifice not visited. Altitude 8,300 ft.	

¹ 1, kaolinite; 2, montmorillonitic clay; 3, hydrous mica; 4, amorphous to poorly crystallized—no readable peaks on X-ray.

Average and extreme concentrations and percentage composition of water from the ephemeral and perennial springs, respectively, are compared in table 2.

TABLE 2.—Concentrations of principal constituents in water from ephemeral and perennial springs

[Data in parts per million except pH]

Constituent or property	Ephemeral springs (15 samples except as noted)				Perennial springs (56 samples)			
	Max	Median	Min	Mean	Max	Median	Min	Mean
SiO ₂ -----	37	13	3.3	16.4	57	21.5	8.8	24.6
Al-----	¹ 1.12	<.02	.00	.03	.19	.02	.00	.018
Fe-----	1.12	.015	.00	.03	.30	.01	.00	.031
Ca-----	7.0	2.6	.8	3.11	26	9.9	1.0	10.4
Mg-----	2.9	.5	.0	.70	6.3	1.0	.0	1.70
Na-----	6.3	2.7	1.2	3.03	15	5.5	.8	5.95
K-----	2.5	1.0	.2	1.09	4.5	1.4	.1	1.57
HCO ₃ -----	42	14	5.0	20	120	51	8.0	54.6
SO ₄ -----	3.6	.6	.0	1.00	14	1.6	.0	2.38
Cl-----	2.0	.2	.0	.50	10	.45	.0	1.06
F-----	² .2	.1	.0	.07	.6	.1	.0	.09
NO ₃ -----	.1	.0	.0	.02	3.0	.1	.0	.28
Dissolved Solids	73	29	11	36	162	72	15	75
pH (lab.)-----	7.5	6.2	5.3	-----	7.9	6.8	5.6	-----

	Percentage composition					
	Ephemeral springs			Perennial springs		
	Max	Min	Mean	Max	Min	Mean
SiO ₂ -----						
Sum of dissolved solids (ppm)-----	59	15	36.4	59	30	45.6
Ca-----						
Cations (epm)-----	71	32	52.5	61	25	40.1
Mg-----						
Cations (epm)-----	31	0	12.1	31	0	13.4
Na-----						
Cations (epm)-----	60	14	30.2	69	25	38.7
K-----						
Cations (epm)-----	14	0	5.0	17	4	7.9
HCO ₃ -----						
Anions (epm)-----	100	44	89.8	100	62	86.9
SO ₄ -----						
Anions (epm)-----	23	0	5.4	25	0	6.2
Cl-----						
Anions (epm)-----	37	0	3.5	21	0	6.3

¹ 10 determinations made.

² 9 determinations made.

The water in the Sierra Nevada has long been used by California's great metropolitan areas—San Francisco, Oakland, and Los Angeles—both because of its abundance and because of its low dissolved-solids content. The water-producing potential of the region is indicated by the map (fig. 1). The isograms (lines of equal runoff) show that

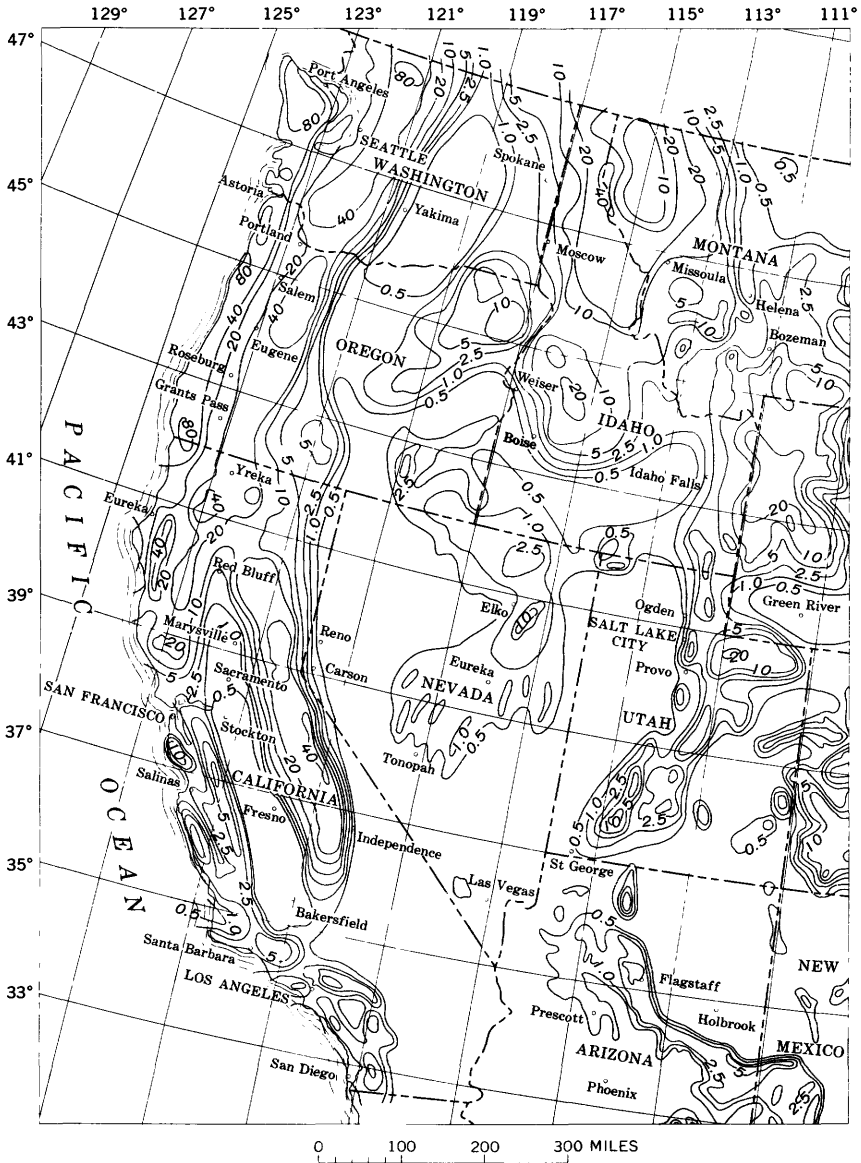


FIGURE 1.—Map of the Pacific Coast region showing lines of equal annual runoff. From Langbein and others (1949).

part of the Sierra Nevada and southern Cascade Mountains yields, on the average, 40 inches of runoff per year and that much of the area yields 20 inches. The rapid decrease in runoff eastward toward the base of the Sierra Nevada and the less abrupt, but appreciable, decrease in runoff westward is also illustrated. A large proportion of the total runoff of the Pacific slope is contributed by the Sierra Nevada and the Cascade Range.

The low mineral content of the water permits use of the Sierra Nevada as a natural laboratory in which some of the relative contributions of mineralization from snow, from the soil, and from the rocks can be discriminated in the water—a procedure that is impossible to follow where water is more highly mineralized.

Large parts of the Sierra Nevada are entirely unpopulated, and most of the remainder of the mountainous area is populated only during the summer months, and then sparsely. It is fairly easy, therefore, to find springs whose waters are free from contamination by human agencies. Waters of this sort were selected for the present study because their chemical composition results entirely from natural agencies and processes.

Results obtained in the Sierra Nevada should have immediate application in other large areas underlain by granitic rocks. Among the many such areas are the Idaho batholith, the southern California batholith, and the large granitic areas of the Front Range in Colorado, the New England States, and North Carolina. In addition, the information provides points of departure from which to evaluate changes in chemical character of water as it moves from source areas progressively downstream into different geologic and hydrologic environments. The downstream water, because of its development, use, and reuse by man, has received much more study than has the source water. Thus, the sequence of chemical changes has commonly been attacked in the middle, and little attention has been given to the source-water areas where processes and products can best be identified because the water has a low concentration of dissolved solids and man's activities interfere little, if at all, with the natural regime.

ACKNOWLEDGMENTS

During the course of the present study, the writers had the benefit of frequent consultations with many colleagues. Special thanks is given to J. G. Schlocker and Ivan Barnes for their help in work with the clay minerals. P. C. Bateman made valuable suggestions based on his long study of granitic rocks of the Sierra Nevada. E. D. Jackson and D. E. White contributed from their experience in geochemistry in many discussions. S. M. Rogers and A. S. Van Denburgh participated in the early parts of the study. The writers are particularly

obligated to R. M. Garrels, who, through correspondence and personal conversations at intervals in the study, supplied guidance and stimulus in the interpretation of the analyses of the waters.

ENVIRONMENT OF THE SPRINGS

CLIMATE

In the Sierra Nevada, as elsewhere, climatic factors influence the chemical character of water. Such factors include the seasonal and geographic distribution of precipitation, the effect of climate on rates and processes of rock weathering, and the chemical character of precipitation, which depends in part on the direction from which a water-bearing air mass moves over the region.

The coastal areas of California are characterized by a typical maritime climate, but inland (Dale, 1959, p. 1-5) the climate is more continental in aspect, having warmer summers, colder winters, and lower relative humidity. The Sierra Nevada is about 100-150 miles from the coast and characteristically has marked wet and dry seasons, the precipitation falling largely during the winter months and normally in the form of snow.

Precipitation, borne by the prevailing westerly winds, in general increases with increasing altitude on the windward slopes of the range up to a point and then decreases to the crest; on the leeward side of the range the precipitation decreases rapidly to the rain shadow near the base. Mean yearly precipitation totals 50 inches or more on parts of the Sierra, especially on the northern part of the range. To the west, however, precipitation diminishes to less than 20 inches on the floor of the Central Valley north of Sacramento and to less than 12 inches south of Modesto. To the east, precipitation decreases to about 12 inches in the vicinity of Reno and to less than 8 inches in the southern part of the Owens River Valley.

Snow in moderate amounts falls in the Sierra above an altitude of 2,000 feet, but only above 4,000 feet does it long remain on the ground. In the middle Sierra the zone of heaviest snowfall is probably at altitudes of 7,000-8,000 feet, not at the highest parts of the range.

According to Thornthwaite (1948, pls. 1A, B), the Sierra Nevada at higher altitudes is characterized by a perhumid (A) climate having large seasonal moisture variations. At lower altitudes the climate is characterized as humid (B), grading very rapidly to moist subhumid (C₂) and dry subhumid (C₁) across the foothills on both sides of the range. Adjacent valley areas are, in Thornthwaite's classification, semiarid (D) and arid (E) within a few miles of the mountain base.

Climatic patterns undoubtedly control rates and types of chemical weathering of the rocks that make up the mountains. For example,

there is some indication (see p. 43) that relative and absolute concentrations of chloride and nitrate in spring water fluctuate seasonally, partly in response to seasonal climatic variations.

GEOLOGIC SETTING

For the purposes of this study, it was necessary to assume that chemical constituents in water might differ according to variations in the mineralogic makeup of rocks through which the water percolated. Knowledge of the geography and geology of the region studied was, therefore, prerequisite.

REGIONAL SETTING

The Sierra Nevada is a range of mountains 300–400 miles long (depending on varying definitions of boundaries with other mountain systems) that trends generally southeast to northwest. Rugged and steep on the east, the mountains rise from altitudes of about 2,500–5,500 feet on the floors of intermontane basins and reach a maximum altitude of 14,496 feet at Mount Whitney. Northward the crestral altitudes are lower—about 8,000–10,000 feet between Yosemite National Park and Lake Tahoe and 6,000–7,000 feet at the north end of the range. The mountains range in width from about 40 to 80 miles and descend westward from the crest on more gentle gradients to the foothill areas of the Central Valley at altitudes of 1,500–2,500 feet.

The broad features of the geology of the region are known partly as the result of reconnaissance mapping done late in the 19th century during the Geological Survey's study of the then valuable placer-gold deposits. Among the contributions made are those of Lindgren (1898, 1900, 1911), Lindgren and Turner (1894), Lindgren and Hoover (1896), Ransome (1898), and Turner and Ransome (1898). Blackwelder (1933), Lee and others (1916), and Reid (1911) added reconnaissance information of broad areas of the Sierra, and Knopf (1918), of the adjacent Inyo Range.

The overall character of the region—a batholith (pl. 1) made up of hundreds of plutons of various sizes, shapes, and mineralogic and petrologic components (Moore, 1959)—has long been established. Overlying the granitic rocks disconformably are a variety of volcanic rocks, many of them andesitic, especially on the western slope (Ransome, 1898; Jenkins, 1951). Eastward from the crest of the range, rhyolitic and basaltic volcanic rocks are more dominant (Gilbert, 1938; Bateman, 1956). The foregoing statements are adequate as generalizations, but the variety of extrusive-rock types throughout the region is large, and the distribution of the rock types is almost as

unpredictable as the distribution of petrologic types among the plutons of the range.

Sedimentary and metasedimentary rocks of various kinds flank the mountains on the western slopes and appear as both large and small roof pendants throughout the plutons. The present study, however, is primarily concerned with ground water from the plutonic rocks.

The 56 nonthermal perennial springs, 15 ephemeral springs, and 8 thermal springs sampled all rise in granitic rocks. Only two of the springs are not in the Sierra Nevada batholith, and those two are in granitic-rock areas associated with the batholith. None of the springs sampled is less than half a mile downslope from known outcrops of volcanic rocks. Some are miles distant from rock types other than granitic.

The perennial springs are distributed throughout the central and northern Sierra Nevada at altitudes ranging from about 1,600 feet to 8,100 feet above sea level; one spring in the adjacent Inyo Mountains is at an altitude of 10,000 feet. Located on both the eastern and western slopes and over a north-south range of about 250 miles, the springs visited are thought to provide a representative and virtually random sampling of the water from the granitic rocks in the region. The ephemeral springs are not so widely distributed and thus are possibly less representative.

GRANITIC ROCKS

As shown by Moore (1959), the plutonic rocks tend to grade from the more calcic types on the west to the more potassic types on the east—that is, from quartz diorite and granodiorite eastward to quartz monzonite, granite, and alaskite. This gradation is, however, a generalization only, and many granodiorite plutons occur near the crest of the range and in the eastern foothills.

Of the perennial nonthermal springs, 18 occur in the more calcic rocks and 18 in the more potassic. The remaining 20 are not differentiated. This separation into groups according to lithology is reflected by symbols on the map (pl. 1) and in the arrangement of analyses reported in table 1.

Two petrologic studies covering extensive areas in the central Sierra are most useful for the purposes of the present report. The rocks of the Yosemite Valley and adjacent areas were described by Calkins (see Matthes, 1930), and those west of Bishop, Calif., by Bateman (1961).

In the present study, the classification used by Bateman (1961, p. 1523) is followed. In this usage, "granitic rocks" contain at least 10 percent quartz and are divided according to the ratio of potassium feldspar (including perthite) to total feldspar, as follows: quartz

diorite, potassium feldspar is 0 to 10 percent of total feldspars; granodiorite, 10 to 35 percent; quartz monzonite, 35 to 65 percent; granite, more than 65 percent. Both Bateman and the present writers found granite, as here defined, to be rare in the Sierra Nevada.

The granitic rocks examined in thin section and by staining techniques (Bailey and Stevens, 1960) in the present study ranged from quartz diorite to quartz microcline gneiss. Microcline was a relatively common member of the potassium-feldspar family although orthoclase was more abundant. The plagioclase family was represented by oligoclase (An_{26} minimum) and andesine (An_{40} maximum), but andesine was predominant. The feldspars composed the greater part of most of the rocks seen, although quartz made up 40 to 45 percent of some specimens. Biotite and hornblende were the only two mafic minerals identified; biotite was more abundant and commonly occurred alone in the quartz monzonite. Allanite, the cerium-bearing epidote, occurred as scattered grains, some of which were large, in a few of the rocks. Magnetite was widely disseminated but was always in small quantities; it characteristically occurred associated with biotite or hornblende or both and commonly appeared to be an alteration product replacing the associated mafic mineral. Titanite (sphene) was a common, but by no means universal, accessory in the rocks.

Among the rocks for which petrographic determinations were made, quartz monzonite and granodiorite number 14 each. Four other rocks were identified as quartz diorite; there were two areas in which quartz microcline gneiss was considered representative of the terrane near the springs; and in one place each the principal rock was granite and alaskite, the latter in the sense of a granitic rock high in potassium feldspar and having almost no mafic-mineral content.

CLAY MINERALS

The results of X-ray diffraction studies of clay-size mineral samples taken in or near the orifices of some of the springs are shown in table 1. The clay minerals were identified so that their effect on the chemical composition of the water might be studied. The results indicate that a variety of clay minerals are present in the environment. Most abundant were poorly crystalline substances which were specifically indeterminable. Locally, however, well crystallized montmorillonite, kaolinite, and micaceous clay minerals were identified. One sample, which was related to an ephemeral spring (analysis 1506, table 1), was apparently pure gibbsite. No other sample showed the presence of gibbsite either alone or in combination with other clay minerals.

The diffraction analyses were made on the <2-micron size fraction of the sediment and, in most samples, on a 2- to 25-micron fraction

also. There was no difference in the kind of clay mineral present in the two fractions. However, the 2- to 25-micron fractions did contain small quantities of feldspar and quartz.

Oriented samples were prepared on glass slides by using standard procedures of dispersion and separation into size fractions. The resulting slides were placed in an X-ray diffractometer for analysis, using nickel-filtered copper radiation (1.54 Å) at 45 kilovolts and 15 milliamperes. The samples were scanned at a rate of 1° or 2° 2-theta per minute. When necessary, X-ray patterns were taken for the following oriented samples: (1) Untreated, (2) treated with ethylene glycol, and (3) heated to 400°C for 1 hour.

The clay minerals were identified on the following basis: Montmorillonite, strong peaks between 12 Å and 15 Å that moved to 17 Å after the sample was treated with ethylene glycol and then to 10 Å after the sample was heated at 400°C for 1 hour; mica, a rational 10 Å series of peaks that showed no variation when the sample was treated with ethylene glycol and heat; and kaolinite, a rational 7 Å series of peaks that showed no variation with treatment of the sample.

Where crystallinity did appear, kaolinite, montmorillonite, or micaceous clay minerals were identified either singly or in combinations of two or all three varieties. Where possible the results were listed (table 1) to show in a general way the relative amounts of the several clay minerals present in the sediment samples. The results indicate that many of the spring waters under investigation were in contact with clay minerals as the water passed through the underground system.

LOCAL SETTINGS OF THE PERENNIAL SPRINGS

Although the waters from springs are considered representative of waters from their respective rock classes, the settings of the orifices of many of the perennial springs are complicated in detail. Some change in permeability of adjacent bodies of rock—even though of the same rock type—is required to cause emergence of ground water. It is unlikely that any springs seen represent seepage from the intersection of an areally extensive water table with the land surface. Typically, points of emergence are related to joint sets, faults, contacts of granitic alluvium over relatively unweathered rock, or of talus overlying massive rock. These conditions—some observed, many concealed—provide zones of lesser or greater permeability and cause the water to emerge at an orifice. The “pure” granitic-rock spring, which is uncomplicated by the presence of alluvium, soil, or other rock types in the immediate vicinity, is so rare as to be nearly nonexistent.

Several springs, the environments of which were examined in some detail, illustrate the generality stated. The setting of “Monitor

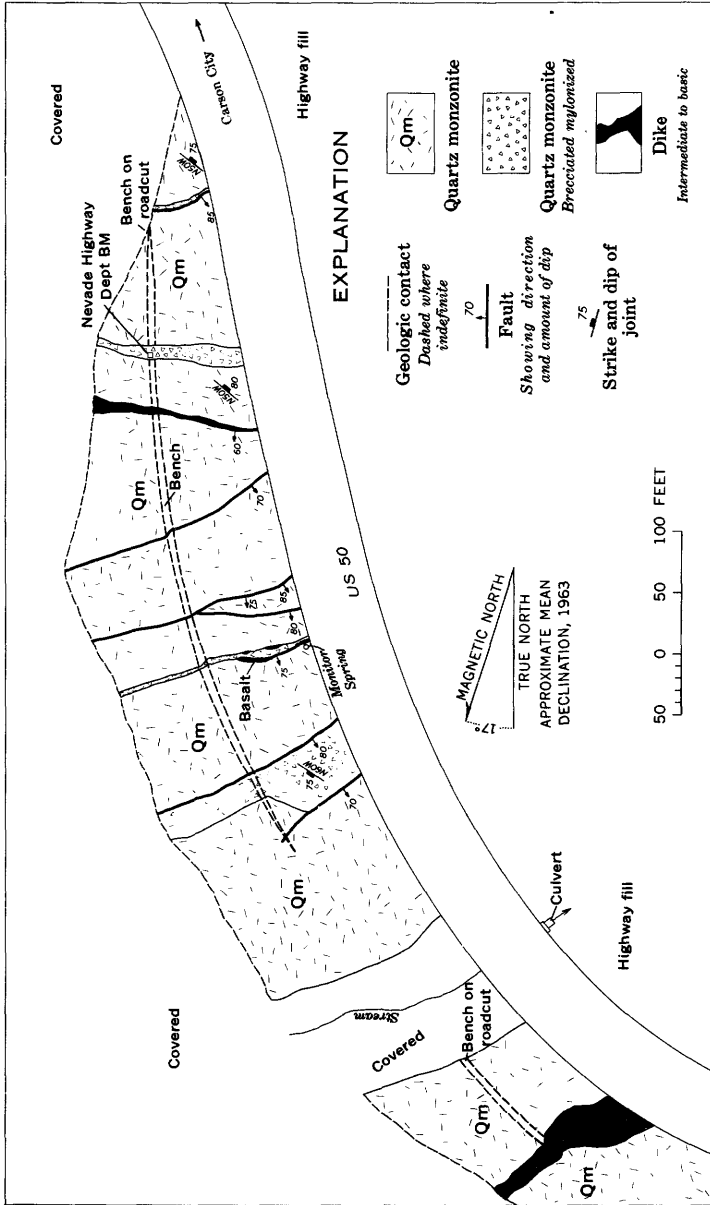
Spring" was studied in greatest detail. "Monitor Spring" (analyses 1131, 1158, 1224, 1330, 1480, 1524, table 1) is near road level on U.S. Highway 50 between Lake Tahoe and Carson City, Nev. The spring is convenient for frequent sampling and is in terrane uncomplicated by human habitation in the drainage area above it. Fieldwork in the present study and mapping by Moore (1961) showed that the terrane tributary to the spring is dominantly quartz monzonite in character. The spring was selected, therefore, for replicate sampling and analysis to provide a record that might be indicative of the seasonal changes in chemical character of a representative water from granitic rocks.

Plane-table mapping (fig. 2) of the large highway cut in which the spring is located and laboratory study showed that the dominant rock is quartz monzonite. According to Moore (1961), the entire mountain area tributary to "Monitor Spring," mapped in reconnaissance, consists of granitic rock. About a quarter of a mile eastward and 350 feet higher on the mountain, the old Kings Canyon Grade, a dirt road that parallels Highway 50 at this place, exposes quartz monzonite for distances of at least half a mile north and south of the spring. Moore's map shows three faults trending northeast in areas close to the spring. The detailed map (fig. 2) shows that "Monitor Spring" is immediately north of a shear zone, perhaps a fault, associated with the group mapped by Moore. Other shear and fault zones that trend east, northeast, and southeast are exposed in the highway cut. Most of the slope above the cut is covered by soil and vegetation.

Northward 450 feet from the spring, an andesite dike ranging in width from about 10 to 40 feet trends northeast. The extension of this dike has been recognized on both sides of the Kings Canyon Grade. About 200 feet south of the spring, a thin southwest-trending basalt dike cuts the country rock. Its extension was not found in Kings Canyon Grade. Even at the spring, thin dikelets of basalt line the about 4-foot-wide fracture zone that is apparently the structure immediately governing the point of emergence of the spring.

With respect to most constituents, "Monitor Spring" water is near the mean concentrations calculated (see table 2) for the entire group of perennial springs. Thus, despite the complications shown in figure 2, "Monitor Spring" is considered representative of perennial springs in the quartz monzonite group.

The geologic setting of three other springs is shown in figure 3. Black Spring (analysis 1259, table 1) is in the NE $\frac{1}{4}$ sec. 15, T. 6 N., R. 16 E., and Poison Spring (analysis 1535, table 1) is in the NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 11 of the same township. Mud Spring was dry when visited. Each of these springs is in a small basin floored with alluvium that overlies and is surrounded by granitic rock identified in the field as



Geology by J. H. Feth, 1961

FIGURE 2.—Sketch map showing geology of area immediately adjacent to "Monitor Spring," SE 1/4 sec. 32, T. 15 N., R. 19 E., Ormsby County, Nev.

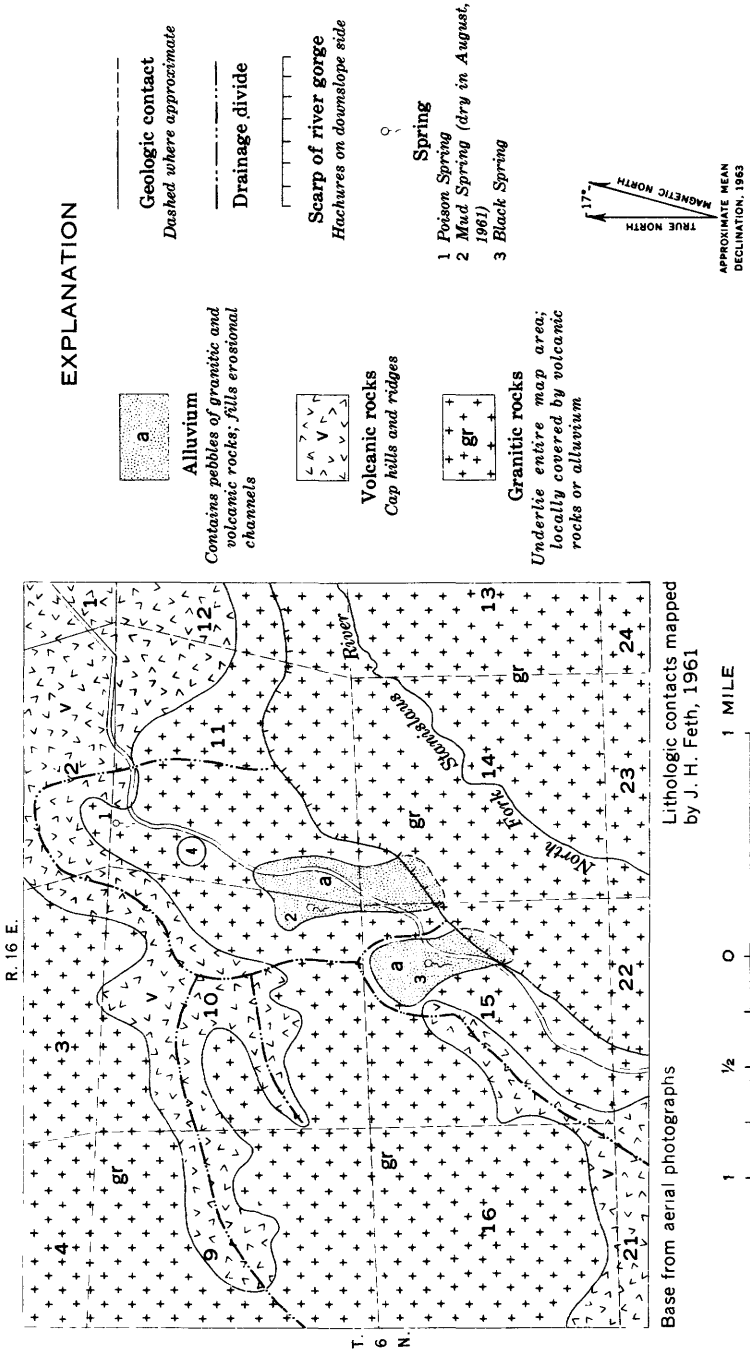


FIGURE 3.—Reconnaissance lithologic map showing environment of three springs in T. 6 N., R. 16 E., Calaveras County, Calif.

quartz monzonite. Nearby ridges are capped with volcanic rocks, and pebbles in the alluvium are more commonly volcanic than granitic. Both Black and Poison springs are low in dissolved-solids content relative to the mean for the perennial springs. The percentage of magnesium in Black Spring is higher than the mean of the group, but that of Poison Spring is less. The higher magnesium percentage of Black Spring water suggests possible influence from the volcanic rocks of the area. In other respects, however, the water analyses conform to the pattern characteristic of the springs.

Another example illustrative of the geologic complexities found at some springs is given in figure 4. As shown in the sketch, three

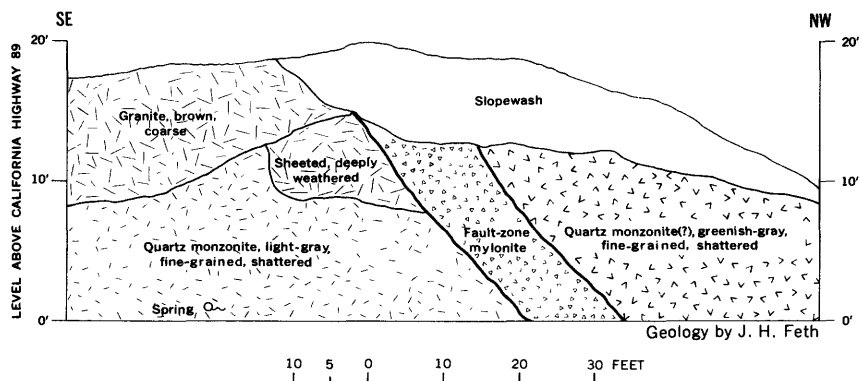


FIGURE 4.—Sketch of highway cut showing geologic relations at an unnamed spring in NE¼ sec. 18, T. 21 N., R. 14 E., near Calpine, Sierra County, Calif.

granitic rock types are displayed in the single roadcut beside California Highway 89 near Calpine. A spring (analysis 1561, table 1) emerges from fine-grained quartz monzonite that is considerably shattered. Overlying the quartz monzonite, possibly in overthrust contact, is a coarse-grained brown granite which is notably sheeted. In the roadcut about 15 feet northwest of the spring is a mylonized zone about 4 feet wide that dips 65° NW. On the side of that zone farthest from the spring is a mass of light greenish gray deeply altered rock that is indeterminable in thin section. X-ray diffraction analysis of this material showed the presence of oligoclase and an abundance of poorly crystallized material; some X-ray peaks suggested the presence of swelling clay, possibly montmorillonite. By analogy with the plagioclase and clay content of other rocks examined, the much-altered rock probably was originally quartz monzonite, although whether from the same rock body as that from which the spring emerges is not known. The water from this spring has a dissolved-solids content of 150 ppm, which is twice the mean for the group of perennial springs, and a sulfate content of 4.6 ppm. In all other re-

spects it conforms in percentage composition to the general pattern of the group.

A few miles west of Monitor Spring is another spring (analysis 1172, table 1) whose geologic setting is shown on figure 5. This spring is

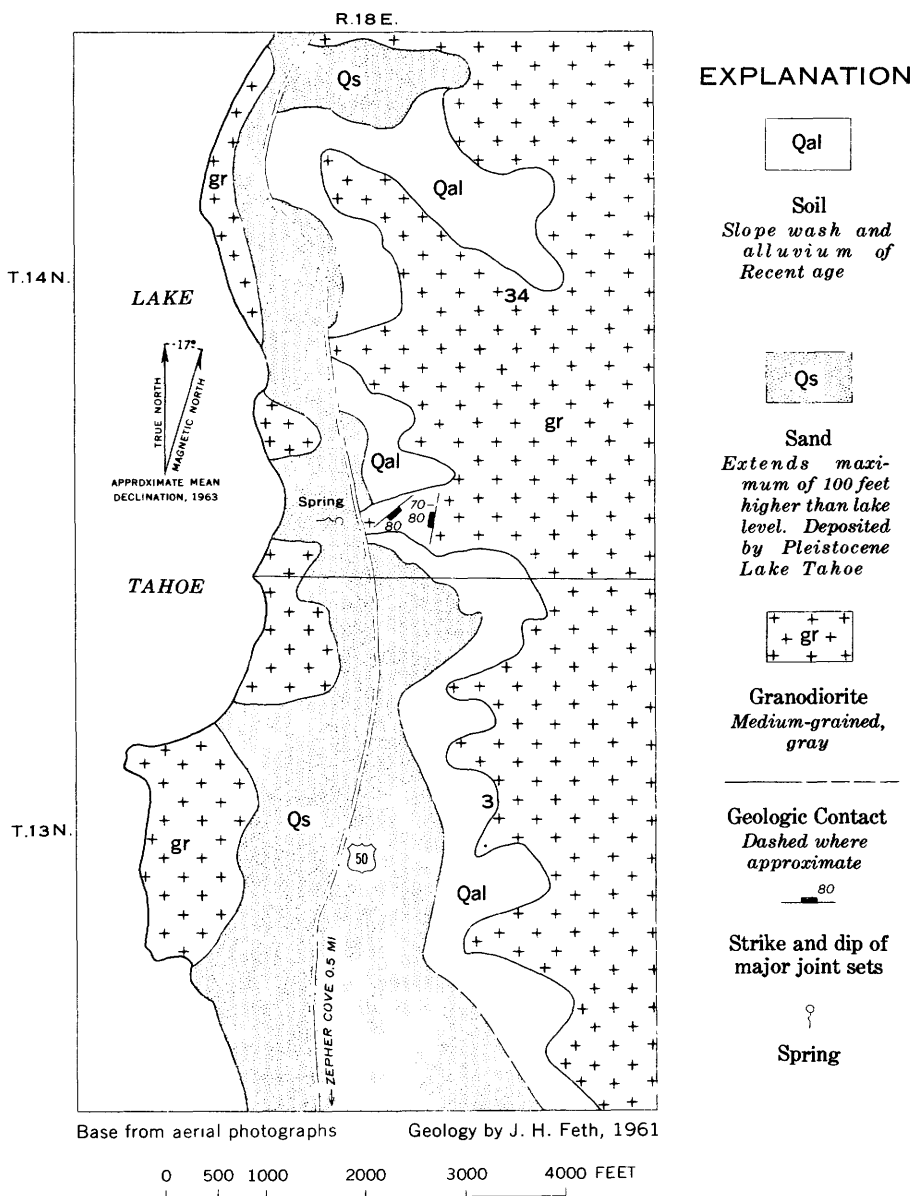


FIGURE 5.—Sketch map showing geologic environment of the spring in SW 1/4 sec. 34, T. 14 N., R. 18 E., Douglas County, Nev.

1½ miles north of Zephyr Cove on the east shore of Lake Tahoe and is used to supply domestic water to a small group of houses. The orifice appears originally to have been in granitic rock and boulders. Thin-section examination and staining techniques show the rock to be granodiorite, and examination in the field indicates that the same rock type prevails in the area of the map (fig. 5). The highway cut immediately east of the spring shows extensive jointing. One set strikes N. 65° E. and dips 80° SE; the other main set strikes N. 10° E. and dips 70° to 80° SE. It is probable that these joints localize points of emergence of the spring water. Highway construction and development at the spring itself, however, have effectively concealed the natural orifices.

The granodiorite hills are flanked on the lakeward side by deposits of Pleistocene age, laid down when Lake Tahoe was at a higher level than the present, and by Recent alluvium. Possibly, therefore, some of the water discharging from the spring has passed through sedimentary materials before reaching the spring. It is also likely (Reid, 1911; Blackwelder, 1933) that faults controlling the eastern margin of the Lake Tahoe basin pass close to the spring. Therefore, a small amount of fault-zone water may be mixed with the dominantly meteoric water discharged. Experience in the Sierra Nevada has shown that water from fault zones commonly carries much more mineralization than does water which has not penetrated as deeply beneath the land surface.

Another geologic setting not illustrated is that of an unnamed spring (analysis 1530, table 1) emerging from joints in granodiorite beside California Highway 108 in the NW ¼ sec. 32, T. 6 N., R. 19 E. There, the country rock is granitic and bears only a light cover of soil and vegetation, and the water emerges directly from the jointed rock; but only 1 or 2 feet from the orifice there is a channel in the granitic surface that is filled with well-bedded tuffaceous sediments enclosing a few granitic cobbles and pebbles. The water is low in dissolved-solids content (29 ppm) and is closely comparable with the water from the group of perennial springs in overall character. It is probable that permeability at the contact between jointed granodiorite and the sediments of the filled channel is sufficiently small that water moving in the joints is inhibited in its passage and finds emergence at the spring.

The examples cited indicate some of the local geologic situations in which the Sierran springs were found. In many places the best that could be determined without extended study was that the spring sampled emerged from granitic talus, or (analysis 1519, table 1) near the toe of a moraine, or from alluvium in areas adjacent to which the exposed rock was granitic. In a few places (for example, analyses

1246-1250, table 1) the orifices were so choked by granitic boulders and cobbles and so overgrown with vegetation—typically alders—that the sample could not be taken from the orifice but was taken from the first available point in the runoff channel. No consistent differences in the chemical character of the waters could be detected resulting from this procedure.

HYDROLOGIC SETTING OF THE SPRINGS

Much of the discussion that follows is devoted to comparison of the chemical behavior of water from ephemeral springs and from the soil on the one hand with that of water from perennial springs on the other hand. This can best be appreciated if the inferred hydrologic similarities and differences in the two systems are borne in mind.

Snow falling on the mountains and later melting furnishes the water that appears at the springs. Snowmelt, locally only a few feet from the parent snowbanks, makes up the soil-water samples which are grouped in this report with the samples from ephemeral springs. It is only during periods of rapid snowmelt that water samples can be obtained from sources such as these. Then the melt water available exceeds the capacity of the underlying granitic rocks to absorb and transmit water, the soil and saprolite become saturated, and ephemeral springs come into being. As the season progresses, snowmelt diminishes in volume and finally vanishes. Then the soil drains to field capacity, and flow from the ephemeral springs ceases for another year.

Snowmelt that has traveled through soil and saprolite, then farther through crevices in the solid rock of the mountains, makes up the samples obtained from the perennial springs. Their perennial nature depends on the capacity of joints and other openings in the rock to store water and to release it slowly throughout the year. Additional storage is provided in local areas where deep rock weathering has produced pockets of saprolite of sufficient size and depth.

CHEMICAL IMPLICATIONS

Water obtained from ephemeral springs probably traveled the few tens to few hundreds of feet between parent snowbank and sampling point in an amount of time ranging from less than an hour to about a day. In a very real sense, however, the time of travel does not represent the entire contact time between water and minerals in the system. During the snowmelt season the soil and saprolite are wet for periods of about 2 to 3 months. During this time, films of water, sometimes frozen at night, adhere to the mineral grains. Weathering in the presence of water, therefore, is a nearly continuous process during the snowmelt season. The soluble products of the weathering are being continuously derived and are available to percolating water

during periods of the day or season when melting is rapid enough to permit movement of water. Some water from snowmelt probably passes through the system from snowbank to collection point rapidly. Some may displace water that has been in contact with the minerals for considerable periods and has acquired a high mineral content. Some may, while passing through the weathered material, acquire part of the mineral content of water films adhering to the rock and soil particles without displacing the water that adheres to the grains.

The same general process may be visualized, with specific differences, for water from the perennial springs. The significant differences include longer travel time during which the water is in contact with rock minerals, the fact that the minerals are continuously wetted throughout the year; and the fact that spring water has been out of contact with the atmosphere for appreciable lengths of time. Water from the ephemeral springs presumably is well aerated during its entire history.

A further process may contribute to mineralization of water from the perennial springs. This is the retardation, with respect to time, of the flow of water through thin cracks in the rock; this retardation is caused by the formation of bubbles of gas on the walls of the cracks. Meyerott and Margenau (1945), using plates of glass that were narrowly separated, made experiments in the laboratory and were able to watch the progressive formation of more and larger bubbles, coincident with reduction of flow of water between the glass plates as time progressed.

Projecting these observations to natural environments, one may visualize water containing dissolved air, including carbon dioxide and oxygen as the active agents, entering the jointed granitic rock. With increasing time of contact between water and rock, more and more reactive bubbles of water-saturated gas would form on the walls of the joint surfaces. Flow would be retarded, and reactions would take place between the minerals of the rocks and the moist gases in the bubbles. As flow continued and the gas content of a particular volume of water was exhausted by reaction, mineralization would increase to a maximum governed by the original volumes of gases dissolved in the water. The process in nature would be, of course, continuous—new gas-charged volumes of water moving into the system and displacing those present earlier.

Under these assumptions, water from the ephemeral springs, being continuously replenished with air and with carbon dioxide from the soil, would remain aggressive with respect to the minerals throughout its time of contact with them. Water moving toward perennial-spring orifices, however, having no renewed supply of air and carbon dioxide, would tend to level off at limits of mineral content imposed by exhaustion of its supplies of reactive gases.

CHEMICAL CHARACTER OF THE WATER AND THE SOURCES OF MINERAL CONSTITUENTS

The average mineral content of snowfall in the Sierra Nevada is 4.7 ppm (parts per million), based on 42 samples that were analyzed in sufficient detail to permit calculation of total dissolved solids. The average mineral content of water from 15 ephemeral springs is 36 ppm, and the average of the 56 perennial springs is 75 ppm. The water samples thus are low in dissolved-solids content, and small changes can be recognized.

It is the purpose of this section of the report to examine by comparison the changes in mineral content that take place as snow melts, as the meltwater passes through soil and saprolite, and then as the water passes through the granitic rocks of the mountains. Where possible, the processes involved and sources of mineral constituents will be described. The analyses of water from ephemeral and perennial granitic-rock sources are presented in table 1, summary data in table 2. Summary data for 79 snow samples are given in table 3.

The discussion is preceded by brief sections describing methods used in assembling and analyzing the data.

COLLECTION OF SAMPLES AND FIELD TESTS

The procedures followed in the collection of water samples were designed to provide the best feasible representation of the chemical character of the water in its natural setting. Containers used were rinsed three or more times with the water being sampled before being filled. A 4-liter laboratory-glass bottle was used for collecting the bulk sample. In addition, a tight-sealing bottle of about 350 ml (milliliter) capacity was filled to within about half an inch of the stopper for use in the determination of pH and alkalinity immediately after opening in the laboratory. Also, a 100 ml sample of water, filtered at the site and stored in a polyethylene container, was taken for determination of iron and aluminum.

At many localities, pH was determined in the field using a portable meter standardized with a buffer solution that had been brought to the temperature of the water being tested. The project was equipped with a truck-mounted field laboratory. Experience has shown that the metal covering of the mobile laboratory provides adequate electrostatic shielding and that values reliable to ± 0.1 pH unit can be obtained if the determination is made within a few minutes after the removal of the sample from the source. Field determinations of alkalinity were also made. Field and laboratory values are shown in adjacent columns in table 1.

ANALYTICAL PROCEDURES

The laboratory procedures for most determinations are those described by Rainwater and Thatcher (1960) and standard in the Quality of Water Branch of the Geological Survey. In a few determinations, however, modifications were made to obtain greater sensitivity. For chloride it was necessary to substitute a more sensitive colorimetric method based on displacement of the thiocyanate ion from mercuric thiocyanate by the chloride ion in the presence of ferric ion. This is a modification of a procedure described by Bergman and Sanik (1957, p. 241).

For silica, aluminum, iron, fluoride, and nitrate, somewhat larger cell sizes were used in the interest of greater sensitivities; for nitrate, larger samples were used. Sodium, potassium, and lithium were analyzed using a hydrogen-oxygen flame spectrophotometer, as was strontium after first being concentrated on a cation exchange resin.

ANALYSIS OF THE DATA

The chemical data accumulated were studied by standard graphic and statistical procedures. In the graphs that follow, the straight line relationships were calculated by the method of least squares. The correlation between variables for which a line of best fit (regression line) is presented was tested statistically by the correlation coefficient (r). The significance of differences between mean values obtained among the several sample populations was evaluated using the t test. The procedures used are those described by Crow, Davis, and Maxfield (1960, p. 152-156, p. 157-158, and p. 57-60, respectively). Other procedures used in data analysis are referenced at appropriate places in the text.

GENERAL CHARACTER

Snow falling in the Sierra Nevada shows diversity in chemical character as is illustrated in figure 6. The more common constituents in natural water are all represented (table 3) in some or all of the samples analyzed. Sodium, chloride, and bicarbonate were detected in most samples, presumably as a result of origin of water vapor over the oceans and, for bicarbonate, of the influence of carbon dioxide in the atmosphere. The history of individual air masses, however, and the influences of dust and gases from continental sources resulted in the wide chemical diversity of individual snows.

Many of the snow samples showed mixture of major cations and anions in roughly equivalent proportions. Other samples, however, were dominantly sodium chloride or sodium bicarbonate in type, and a few were calcium magnesium bicarbonate type. Some of the details of the chemical character of the snow were discussed by Rogers and Feth (1959), and Feth and others (1962).

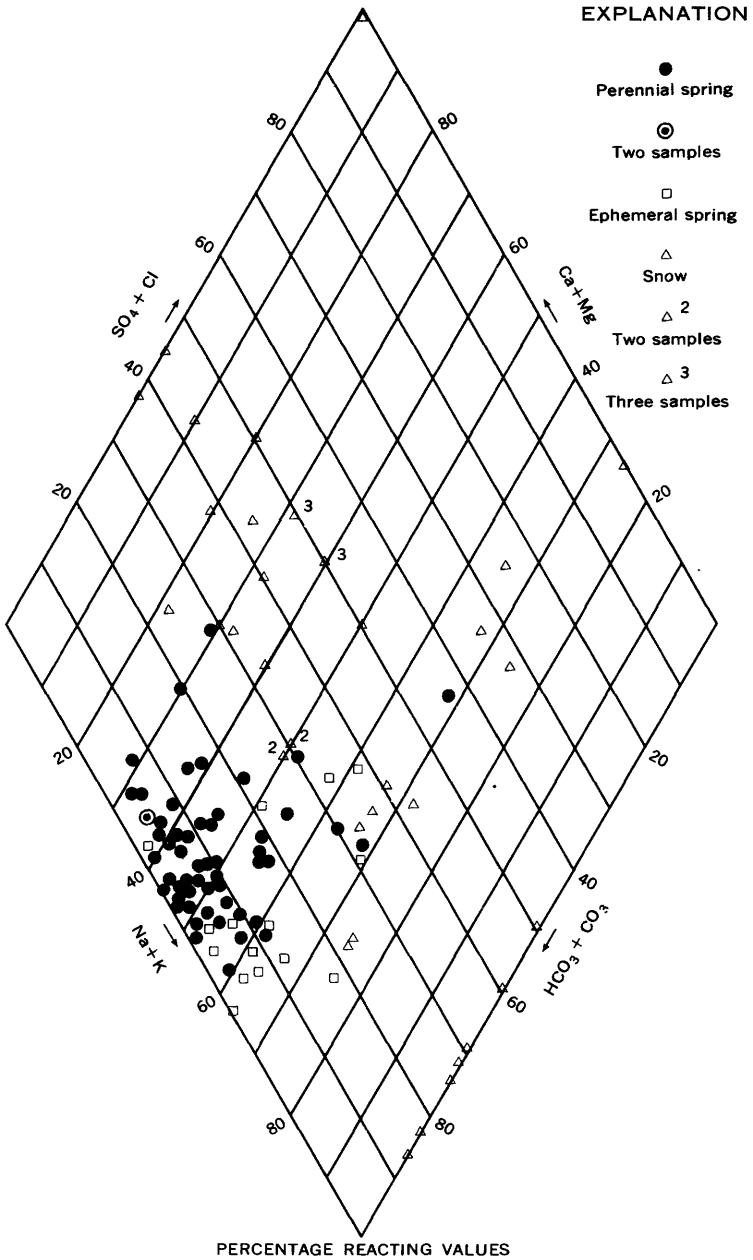


FIGURE 6.—Diagram showing general chemical character of perennial and ephemeral springs and of snow.

TABLE 3.—Concentrations of principal mineral constituents in Sierra Nevada snow samples

[Adapted from Feth and others (1962) ¹]

Constituent	Concentration (ppm) ²			Number of determinations
	Maximum	Mean	Minimum	
Silica (SiO ₂).....	1.7	0.16	0.0	52
Calcium (Ca).....	3.8	.40	.0	42
Magnesium (Mg).....	.5	.17	.0	42
Sodium (Na).....	1.6	.46	.1	71
Potassium (K).....	1.5	.32	.0	67
Bicarbonate (HCO ₃).....	9	2.88	.0	69
Sulfate (SO ₄).....	5.3	.95	.1	51
Chloride (Cl).....	1.6	.50	.0	79
Nitrate (NO ₃).....	.3	.07	.0	55
Dissolved solids.....	14	4.7	.9	42

¹ Includes unpublished data in files of Geological Survey.² Approximate sensitivities, in parts per million, of the determinations are as follows: SiO₂, 0.2; Ca and Mg, 0.25; Na and K, 0.01; HCO₃, uncertain, varies with pH and concentration; SO₄, Cl, and NO₃, 0.1.

As soon as the snowmelt comes in contact with the lithosphere, however, the diversity largely disappears. Water from the ephemeral springs is characteristically the sodium bicarbonate type or mixed-cation bicarbonate type. The grouping of points representing ephemeral sources (fig. 6) is fairly tight, and the consistency in overall chemical character is apparent. As contact with the lithosphere continues, the chemical character of the water changes again. The points (fig. 6) representing water from perennial springs show the increased significance of calcium and magnesium among the cations. With only two exceptions, however, bicarbonate continues to make up 70 percent or more of the anions.

The strong dependence of total dissolved-solids content on bicarbonate and silica is shown graphically in figure 7. In water from ephemeral sources, the silica content is proportionately larger than that in perennial springs. In both groups the percentage of calcium and magnesium among the cations also tends to increase with increasing dissolved-solids content. The coefficient of correlation is significant at levels of confidence in excess of 0.01 for all the relations shown on the graph. That is, there is less than 1 chance in 100 that the relationships result from chance. They may confidently be considered to be real.

PROGRESSIVE INCREASES IN MINERALIZATION

On the average, the mineral content of the water increases 7½ times as snow melts and the melt water moves through the soil and saprolite. The average concentration doubles again as water moves toward the orifices of the perennial springs.

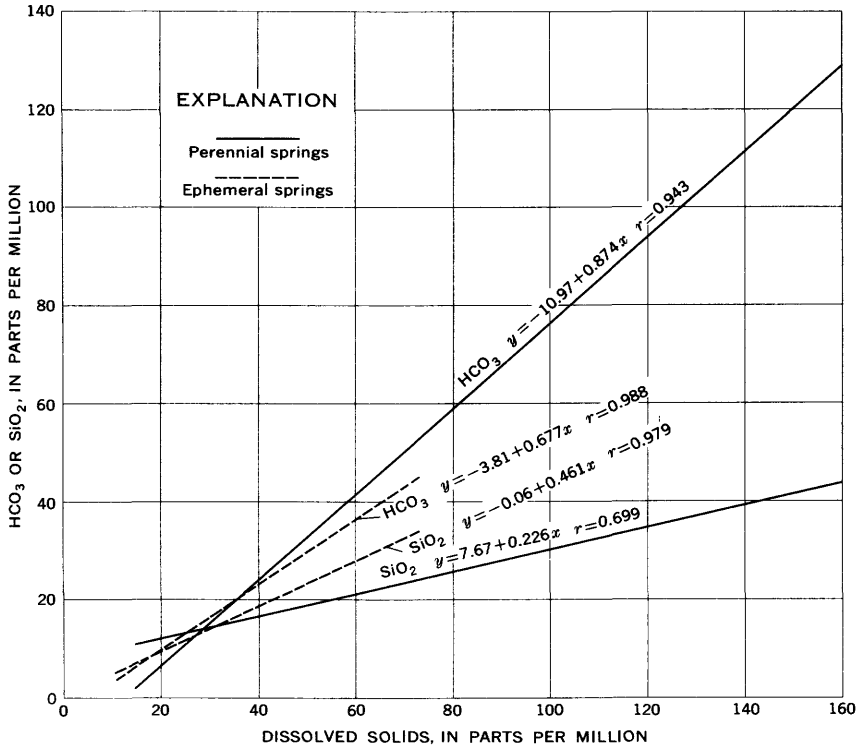


FIGURE 7.—Graph showing relation between dissolved-solids content and selected constituents in water from perennial and ephemeral springs.

Silica is not only abundant in the rock minerals but is abundantly and readily available for solution in the presence of water. The mean silica content of the snow is 0.16 ppm; that of the ephemeral springs is 16.4 ppm, which represents an increase of 100 times. No other constituent has nearly so large an increase. The average silica content of the perennial springs, 24.6 ppm, is 1½ times that of the ephemeral sources and about 150 times that of snow.

Calcium shows the next largest increase. The ephemeral springs have nearly 8 times as much calcium, on the average, as the snow; and the perennial springs have 3½ times as much calcium as the ephemeral sources, or 26 times as much as the snow. These and other comparisons are given in table 4. The chemical behavior of individual constituents in relation to the environment will be discussed in following sections of this report.

TABLE 4.—Changes in average concentration of selected constituents in snow, ephemeral springs, and perennial springs

Constituent	Ratios of average concentrations		
	Ephemeral springs	Perennial springs	Perennial springs
	Snow	Ephemeral springs	Snow
Silica (SiO ₂)	100	1.5	154
Calcium (Ca)	7.8	3.5	26
Magnesium (Mg)	4.1	2.4	10
Sodium (Na)	6.6	2.0	13
Potassium (K)	3.4	1.4	4.9
Bicarbonate (HCO ₃)	7.0	2.7	19
Sulfate (SO ₄)	1.0	2.4	2.5
Chloride (Cl)	1.0	2.1	2.1
Nitrate (NO ₃)	.3	14	4.0

CONCENTRATION BY EVAPORATION

Evaporation from lakes in the region may range from less than 30 inches annually in the High Sierras to about 45 inches in the foothills, according to Kohler and others, (1959, pl. 2). Mean yearly precipitation was shown by Dale (1959, p. 25, 36) to range from 72 to 16 inches. The potential concentration by evaporation, therefore, is large.

Comparison of average concentrations of major constituents in snow with average concentrations in water from seven lakes in the Sierra Nevada showed that the lake water contained 22 times as much silica as the snow, 3½ times as much calcium, about 2½ times as much bicarbonate, but only 0.6 as much magnesium and chloride. Sodium content in lake water was twice that in snow. Potassium and sulfate showed virtually no change in concentration.

The comparisons given in table 4 show an even larger spread in average change of concentrations as snow melts and enters soil and saprolite. The influence of the lithosphere seems to mask the effect of evaporation effectively, and no firm estimate of concentration by evaporation is warranted from the data on hand.

QUARTZ MONZONITE AND GRANODIORITE GROUPS

The average chemical character of spring water from quartz monzonite and granodiorite is given in table 5. The only appreciable differences apparent in the mean concentrations are in calcium, sodium, and chloride. Examined using the *t* test, the difference in chloride means has significance at about the 0.05 level. The differences in means of sodium and calcium, when examined statistically, may be the result of chance.

TABLE 5.—*Comparison of concentrations, in parts per million, of major constituents in water from quartz monzonite and granodiorite*

Constituent	Quartz monzonite ¹			Granodiorite ²		
	Max	Mean	Min	Max	Mean	Min
SiO ₂ -----	57	26.2	11	53	26.2	8.8
Ca-----	26	9.8	1.6	24	8.3	1.0
Mg-----	4.2	1.5	.0	6.3	1.5	.0
Na-----	13	5.4	1.5	15	6.7	.8
K-----	2.5	1.5	.4	4.5	1.5	.2
HCO ₃ -----	109	49.8	10	120	47.7	8.0
SO ₄ -----	14	2.8	.0	9.9	2.7	.0
Cl-----	3.2	.7	.1	10	2.1	.0
Sum of dissolved solids-----	150	72.7	21	154	73.0	15

¹ The 18 samples include 1 each from granite and alaskite and 2 from quartz microcline gneiss.

² The 18 samples include 4 from quartz diorite.

Rocks of the quartz monzonite and granodiorite groups in the Sierra Nevada are markedly similar, both groups commonly containing andesine (An₃₀₋₄₀) as the principal feldspar. Among the mafic minerals, biotite and hornblende occur in both rock types, although the hornblende content is more obvious in the granodiorite group. It is not surprising, therefore, that the waters from the two groups should be chemically similar, especially if plagioclase feldspar and hornblende are the principal contributors of dissolved solids to the water.

The difference in chloride content is probably a reflection of structure rather than of rock composition. Many of the springs in the granodiorite group are in places where nearby faulting may reasonably be inferred. Thermal-spring water contains significantly greater amounts of chloride than does nonthermal water in the Sierra Nevada. As the thermal springs are related to faults, small amounts of water having a relatively high chloride content may be rising in fault zones to mix with the nonthermal water of some of the springs from granodiorite, thus increasing the chloride content of the spring water.

SOURCES, PRODUCTS, AND PROCESSES

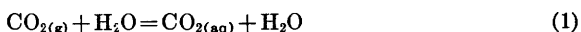
Activity of the hydrogen ion seems to control the ability of the water to derive mineral constituents from the rock. The process was explained by Frederickson (1951) as penetration of the H⁺ ion into the lattice of the mineral. There the electrical neutrality of the molecule is upset, and an atom of one of the metals is displaced from the molecule to compensate for the entering H⁺ ion. Silica is also released by the reaction, the crystal is expanded, progressively more surface area is exposed as a result, and the chemical activity of the system is increased. Simple solution doubtless also contributes to mineralization of the water.

In the Sierran water, virtually the only source of inorganic acid—therefore the major source of H^{+1} ions—is the reaction of carbon dioxide with the water to form carbonic acid. Thus carbon dioxide promotes the reaction of water with rock-forming minerals. Many of the other relations observed among individual mineral constituents depend mainly on H^{+1} ion penetration for their inception.

CARBON DIOXIDE SYSTEM

The action of carbon dioxide in the weathering processes is emphasized by the relation of bicarbonate to total dissolved solids shown graphically in figure 7. The graph suggests that, beyond a minimum of unknown duration, the time of contact between rock and water may not be so significant as the carbon dioxide content in determining the mineralization of the water. This inference is based on two assumptions: (1) the water of the perennial springs spent the bulk of its time underground in a system closed with respect to the soil and atmosphere, and (2) the initial partial pressure of carbon dioxide resulted from the carbonic acid acquired during contact with the atmosphere and, more significantly, the soil, before the water entered the closed system. The P_{CO_2} (partial pressure of carbon dioxide) of the soil is said (Bear, 1955, p. 205) to be from 10 to more than 300 times that of the atmosphere.

The relation between P_{CO_2} and the chemical reactivity of water through its H^{+1} ion content is shown in equations 1, 2, and 3 below.



The increasing capacity of water in the Sierra Nevada to react with rock-forming minerals as it progresses through the chain of events from precipitation through runoff to ground water is largely expressed by the average bicarbonate contents of the several groups of samples—snow, less than 3 ppm bicarbonate; ephemeral springs (equivalent to runoff), 20 ppm; and ground water at the perennial springs, nearly 55 ppm. The soil must be the source of virtually all the carbon dioxide content in the water in excess of that contributed by the atmosphere. The greater average content of carbon dioxide (as bicarbonate) in the water from perennial springs probably implies longer contact between that water and soil than prevails between soil and the water of the ephemeral sources.

SILICA AND THE CATIONS

Even as bicarbonate content is correlated with total mineralization of water in the Sierra Nevada, so in the early stages of the transition from melting snow to ground water, silica is overwhelmingly conspicuous by its abundance and rapid increase in concentration.

Actually the proportionate increase of silica (table 4) from its concentration in snow to that in ephemeral spring water is four times the increase in bicarbonate in the same comparison. This seeming discrepancy results, of course, from the small concentration of silica in snow and from its great abundance and ready availability in the geologic environment of the Sierra Nevada.

It is noteworthy, nonetheless, that for every mole of bicarbonate in solution, nearly one mole of silica is released until a first limit of about 20 ppm silica is approached. This 1:1 mole ratio extends throughout the range of concentration of most of the ephemeral sources and is shown graphically in figure 8. In water from the perennial springs, the nearly 1:1 ratio persists in some samples to silica concentrations of about 50 ppm. In others, where bicarbonate exceeds 40 ppm, the content of silica levels off at limits between 20 and 30 ppm.

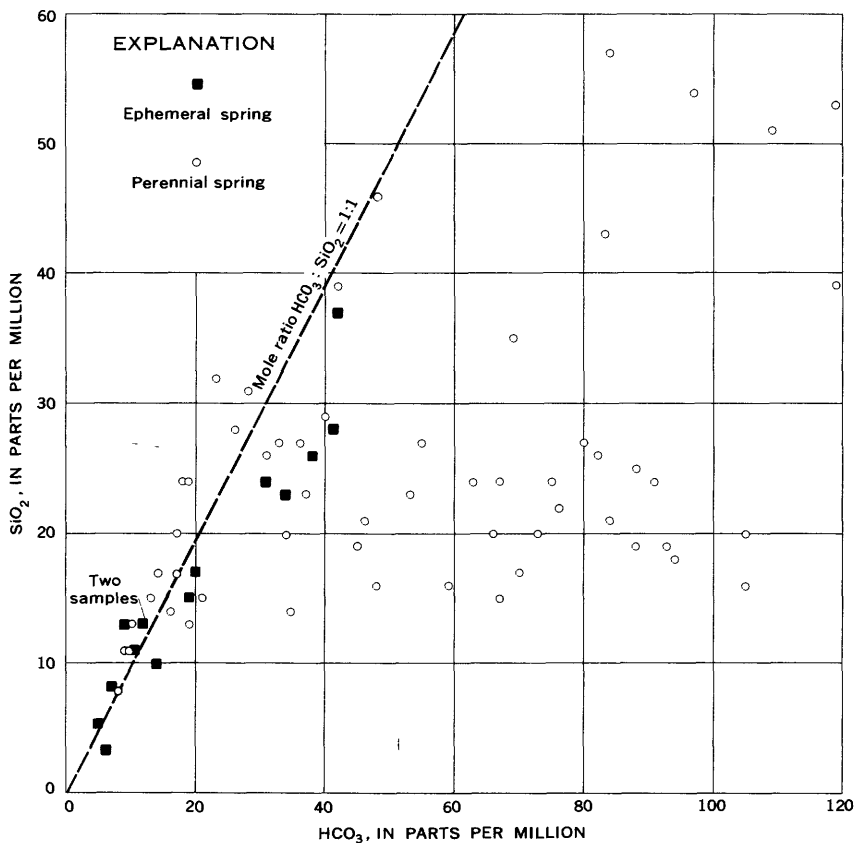


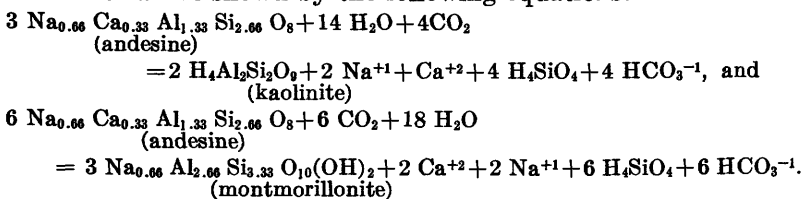
FIGURE 8.—Plot showing relation between bicarbonate and silica content in water from ephemeral and perennial springs.

These relations suggest the possibility that two types of reactions involving silica take place in the systems under study. The overall correlation between content of silica and total mineralization in both ephemeral and perennial spring water (fig. 7) implies that some silica is released from the minerals so long as reaction between water and rock continues.

The first type of reaction, that which yields a 1:1 mole ratio of silica and bicarbonate, may result from release of silica during hydrolysis as hydrogen ions displace cations from the lattice of the minerals. On the other hand, X-ray diffraction studies (see table 1) of clay-size weathering products showed that there is an abundance of amorphous to poorly crystalline material, much of which may be siliceous, in the geologic environment. As amorphous silica is generally considered to be more soluble in water than is crystalline silica or the silicate minerals (Hem, 1959, p. 53-57), the second possible type of reaction may be the direct attack of snowmelt water on the amorphous residues of mineral weathering that are abundant near the land surface.

Support of the first hypothesis involving hydrolysis of fresh mineral grains appears in relations observed between silica and the cations found in the water. More than half the samples from the perennial springs and 12 of the 15 samples from ephemeral springs have (fig. 9) a 2:1 mole ratio of silica with respect to sodium. A group of samples show a 1:1 mole ratio of silica with respect to sodium. The mole ratio of silica with respect to potassium is about 13:1; that of silica with respect to calcium is about 5:1 and has considerable scatter of the points when plotted.

The initial mole ratios of silica to sodium (2:1) and of silica to bicarbonate (1:1) suggest the formation of kaolinite and montmorillonite or both during weathering of the plagioclase feldspars. These reactions can be shown by the following equations:



The X-ray diffraction data (table 1) show the presence of well-crystallized clay minerals at some localities. The weathering of plagioclase feldspar to form montmorillonite or kaolinite and the formation of mica during weathering of potassium feldspars readily accounts for the presence of these clay minerals in the environments of the springs. The same reactions presumably release to the water that content of sodium and potassium that is not attributable to concentrations of those ions in melting snow.

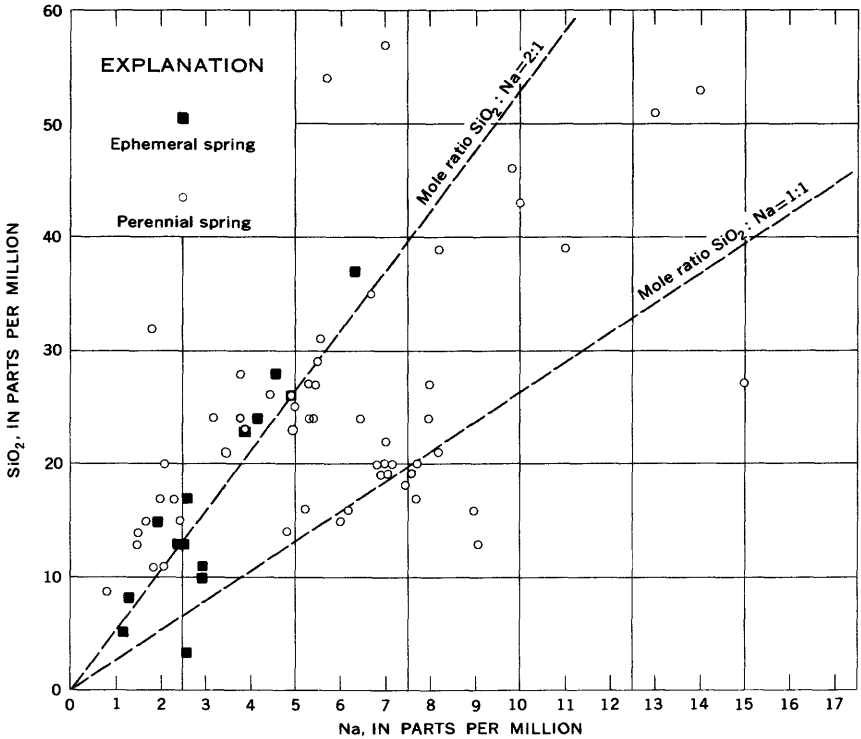


FIGURE 9.—Plot showing relation between sodium and silica in water from ephemeral and perennial springs.

The reactions proposed above involve only water and the minerals that are known to be present in the rocks and soil in the Sierra Nevada. The details and controls of the processes are unknown.

The decrease in percentage of sodium and potassium among the cations with increasing mineralization of the water stems from the fact that, with only four exceptions, the content of sodium in the water does not exceed a limit of 7.0 ppm, and in only five samples does the content of potassium exceed 2.5 ppm. In samples having a low mineral content, the sodium and potassium increase approximately linearly toward the limits named. These limits may be imposed by decrease in the ability of water to attack feldspar once the initial content of carbon dioxide has reacted with the minerals (R. M. Garrels, written communication, 1961). The lessened activity of hydrogen ions remaining then may still suffice to release calcium and magnesium from the less resistant hornblende and biotite.

Calcium and magnesium contents increase with increasing mineralization without respect to any limits within the systems studied. The nearly perfect linearity of the increase is such as would be expected in water that dissolves increasing amounts of mineral matter from

carbonate rocks. The suggestion (R. M. Garrels, written communication, 1961) that calcium and magnesium in the water is derived from secondary carbonate minerals is attractive. There is, however, no field or laboratory evidence that carbonate minerals are present; they have not been seen coating joint surfaces nor detected as interstitial deposits during thin-section examination of deeply weathered rock in this study, nor in generally fresher rock slices examined by others (P. C. Bateman, oral communication, 1962). The plagioclase feldspar, hornblende, and biotite therefore remain the identified probable sources of calcium and magnesium.

CHLORIDE, SULFATE, AND NITRATE

The water of the Sierra Nevada is notably low in contents of chloride, sulfate, and nitrate. The behavior of each of these anions, however, is of more than ordinary significance because of the geochemical implications involved. These anions in the water are derived largely from the atmosphere, from admixture of fault-zone water, or, for nitrate, from the soil. The rocks contribute only small additional amounts. Chloride and sulfate seem actually to be removed from solution by adsorption in some circumstances. Chloride and nitrate contents fluctuate seasonally, and inversely, in water from one spring sampled at intervals over a period of 2 years. The inferred removal of chloride from solution inhibits its usefulness as a geochemical tracer in areas where adsorption may occur.

SOURCES OF ANIONS

The average chloride and sulfate contents of snow and of the ephemeral springs is the same—0.5 ppm and 1.0 ppm, respectively. The average content of chloride in the perennial springs is about 1.0 ppm, and the average content of sulfate is 2.4 ppm. The median values in water from the perennial springs, however, are chloride, 0.45 ppm, and sulfate, 1.6 ppm. The weathering of the rocks seems to add but little to the concentration of these ions.

The granitic rocks of the Sierra Nevada contain very little pyrite—in fact, none was seen in the present study—nor are there other sources of sulfur in appreciable amounts in the minerals. The small increase in average sulfate content, therefore, is explained by the mixture, in some localities, of water rising in fault zones with water derived more directly from the melting snow. The samples showing higher concentrations of sulfate were obtained in places where nearby faulting is known or can reasonably be inferred.

The larger concentrations of chloride in all the perennial springs except Cold Spring were also found where faults are known or can be inferred. At Cold Spring (analysis 1567, table 1), within a public campground, the possibility of contamination is present.

Inasmuch as thermal fault-zone water in the Sierra Nevada is known to have appreciably higher concentrations of both chloride and sulfate than does the nonthermal water, the mixture of the two seems to explain the occurrences of chloride and sulfate in the perennial springs that cannot be attributed to the initial content in melting snow or to the very minor contributions made by weathering of the rock. The chloride made available by weathering of the granitic rocks of the Sierra Nevada is probably restricted to that in aqueous inclusions in mineral grains and to that which replaces OH^{-1} and O^{-2} in biotite, as described by Kuroda and Sandell (1953, p. 889).

The main source of nitrate in the water seems to be biologic activity in near-surface zones—forest litter and the soil. The average nitrate content of the snow is 0.07 ppm, and that in the perennial springs is about 0.3 ppm. The fault-zone water does not, for this element, seem to supply the difference noted, nor does the granitic rock offer a likely source.

The nitrogen content of granites was reported by Wlotzka (1961, p. 112). In 17 samples, the average content as $\text{NH}_3\text{-N}$ (ammonia nitrogen) was 18 grams per ton, equivalent to 18 ppm. Of this amount, 7.2 ppm, on the average, was water soluble. Converted to NO_3 (nitrate) and expressed as a ratio, this is equivalent to one part NO_3 in 38,000 parts of rock (1:38,000). The average nitrate content of the spring water is about 0.3 ppm, and the average dissolved-solids content is 75 ppm. Subtracting the average content of carbonate species and assuming that the remainder of the mineralization is derived entirely from rock minerals, the ratio NO_3 :dissolved solids is 1:160. The rock, therefore, cannot be considered as a major source of nitrate if Wlotzka's values are applicable to Sierra Nevada granitic rocks. The activity of soil bacteria and the decay products of fallen vegetation are the probable sources of most of the nitrate found in water from the springs.

ADSORPTION OF CHLORIDE AND SULFATE

The removal of both chloride and sulfate from solution in water in the Sierra Nevada is strongly suggested by the data. The average concentration of both constituents in water from the perennial springs is about twice the average concentration found in snow. Of the perennial springs, however, 7 have a chloride content equivalent to the average content in snow, and 28 have less. Two perennial springs have a sulfate content equivalent to the average content in snow, and 36 have less.

The median concentration of chloride in snow is 0.4 ppm; in the perennial springs the median is 0.45 ppm. Samples from 25 springs had smaller concentrations of chloride than the median value found in snow.

The median concentration of sulfate in snow is 0.7 ppm, and in the perennial springs, 1.6. Samples from 15 springs had sulfate concentrations less than the median value for snow. Of these, 8 samples had no determinable sulfate, whereas every one of the 51 snow samples analyzed for sulfate showed determinable amounts.

Even if weathering of the rock minerals yields no chloride at all to the water, it is still necessary to assume that the water commonly moves from parent snowbank into the aquifers and emerges at the springs without any concentration by evaporation—in some spring water, the chloride content is apparently reduced. The chloride content of the snow samples ranged from below the limits of detection (reported 0.0) to 1.6 ppm. The differing chloride contents of the spring water in the range less than 0.5 ppm might, therefore, be assigned to recharge, without concentration by evaporation, from bodies of snow having chloride concentrations appropriately less than 0.5 ppm. There was, however, no significant regional consistency in the distribution of the low-chloride snow, nor of the low-chloride springs. Furthermore, the required assumptions, (1) no concentration by evaporation and (2) no contribution of chloride from rock weathering, are only dubiously tenable.

The same lines of reasoning hold in general with respect to sulfate. The ability of kaolinitic clay to adsorb anions provides an explanation for the anomalous behavior of chloride and sulfate, and kaolinite has been identified in the geologic environments of some of the springs.

One hundred grams of kaolinitic clay can adsorb 0.3 meq (milliequivalents) of chloride at pH 6.7; 1.1 meq Cl^{-1} at pH 6.1; and 2.4 meq Cl^{-1} at pH 5.8 (Bear, 1955, table 4.4, p. 140). Soils have a greater capacity to adsorb Cl^{-1} than do pure clays because of the sorptive capacity of hydrous oxides of iron and aluminum that are present (Bear, 1955, p. 141). That numerous springs have a chloride content that is less than the mean content of the snow suggests that chloride sorption may be of common occurrence in the Sierra Nevada.

A corollary of this conclusion, if valid, is that chloride concentration, where small, is not a valid criterion on which to build in determining dilution or concentration resulting from mixing of waters from several sources. Nor is the hypothesis that chloride moves through the system without chance of removal necessarily always valid. The restriction of sorption to environments having pH below 7.0 should, however, be kept in mind. According to Bear, no sorption of chloride on kaolinite takes place where the pH is higher than about 6.7.

Also, according to Bear (table 4.4), the sorptive capacity of kaolinitic clay is greater for sulfate than for chloride. Even at pH 6.9, 100 grams of the clay can adsorb 0.7 meq of sulfate; and at pH 6.25, the stated sorptive capacity is 4.6 meq of sulfate. The probability of

removal of sulfate by adsorption in favorable environments also seems to be real.

SEASONAL VARIATIONS OF CHLORIDE AND NITRATE

The record of "Monitor Spring" (fig. 10) is of special significance because chloride and nitrate concentrations vary from season to season. The concentrations of most constituents showed only minor variations. The seasonal periodicity of chloride and nitrate has at least two major implications. The first is that in the "Monitor Spring" system there is one time in the year during which the percolating water receives a short-lived "slug" of nitrate. The second implication is that water reaches "Monitor Spring" about 6 months after entering the recharge area, assuming a minimum travel time—the period might equally well be 18 months, on the basis of present data.

These inferences are based on several considerations. The drainage area contributing to the spring is not inhabited, nor is it used for pasture. It is rather well covered by both conifers and deciduous trees, shrubs of several varieties, and some grass. As melting snow provides the main supply of water to the aquifer, it is in the spring of the year that the decay products from vegetation of the preceding year would most readily be carried into the aquifer; but it is approximately half a year later that the nitrate content of the water increases. From the nature of the point of emergence, the flow from the spring is somewhat diffused and is not measurable with accuracy. However, the measurements and estimates that have been made indicate that the discharge is greater in the late summer and early winter than in the spring, thus again suggesting a lag of about 6 months (or some odd-numbered multiple thereof) between recharge and discharge.

If the higher nitrate contents reflect periods of recharge from rapid snowmelt as postulated, then the chloride content at equivalent times (0.4 ppm in each of three samples) may be equivalent to the chloride content of the snow, little concentrated by evaporation. Later in the season, as recharge diminishes in rate, the recharging water may be somewhat concentrated by evaporation and yield the higher values observed. The virtual constancy of concentration of constituents such as silica, calcium, and sodium, however, do not suggest significantly different seasonal rates of derivation of the major constituents in the water.

If vegetative decay provides large amounts of nitrate to melting snow, the same process may release organic acids in quantities sufficient to cause lowering of pH in the water available for recharge. At lower pH, as was pointed out earlier, the capacity of kaolinitic clay to adsorb chloride is increased. Thus, the lesser chloride content with higher nitrate content may result from chloride sorption. At present there is no direct evidence to support either hypothesis.

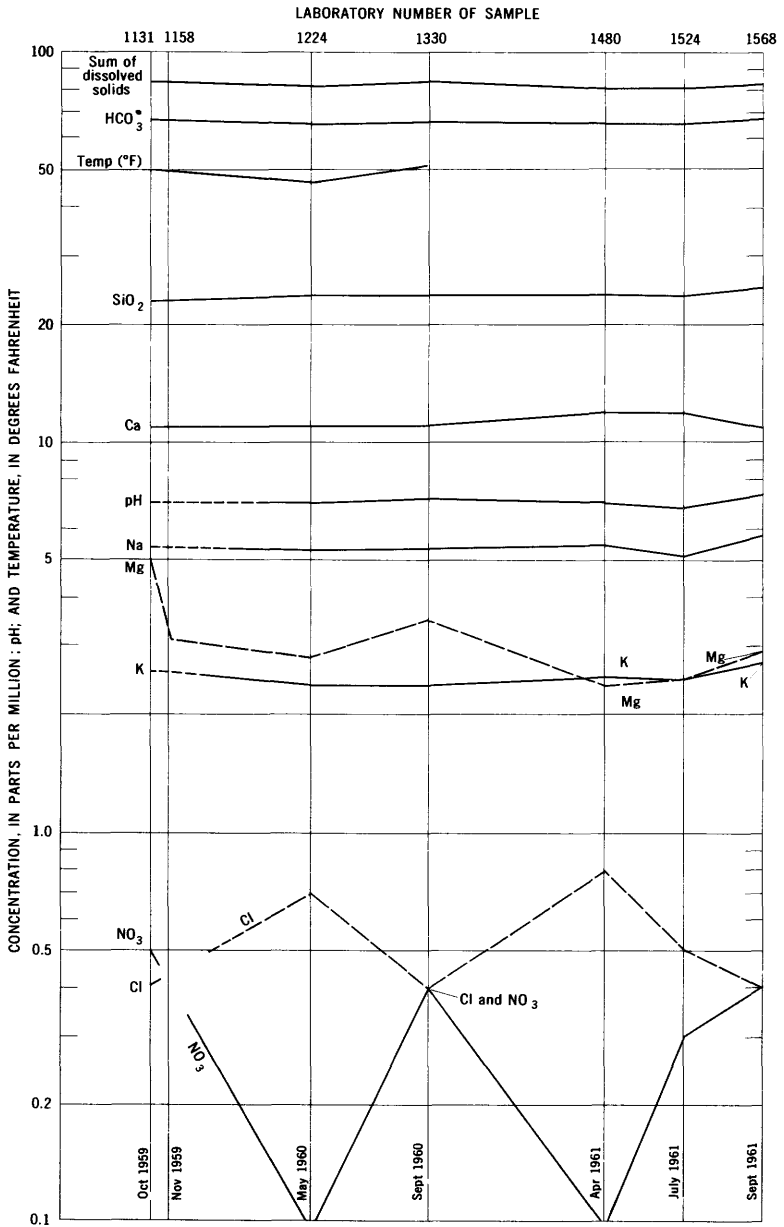


FIGURE 10.—Graph showing seasonal variations in concentrations of selected constituents in water from "Monitor Spring."

Whatever the ultimate explanation, the phenomenon of inverse relations between chloride and nitrate concentrations in surface waters has been reported elsewhere, although no known previous observations

are recorded for ground water. Streams in Indiana and Virginia that were sampled by Slack (1955, p. 23, 28–29; 1962, written communication) showed an initial rise in nitrate concentration in early winter and a progressive decrease throughout the spring. Decaying deciduous leaves were cited as the principal source of nitrate. In 10 streams of the San Francisco Peninsula, Calif. (Feth, 1961), higher concentrations of nitrate resulted as winter rains accumulated the products of decaying summer vegetation and carried them into the streams. Gorham (1957a, p. 24; 1957b, p. 153) reported comparable observations in English and Scottish lakes; and Dugdale and Dugdale (1961) reported seasonal variations in nitrate content of lakes on Afognak Island, Alaska, and attributed the increases to decay of alder leaves which are abundant in certain of the lakes' tributary streams. Present evidence seems to favor decaying vegetation as the main source of nitrate in Sierran ground water.

RELATIVE MOBILITY OF THE COMMON ELEMENTS AND IMPLICATIONS AS TO WEATHERING

In general, rocks of diverse petrologic makeup and their weathering products seem to offer all the metallic constituents and the silica commonly found in natural water in amounts exceeding the capacity of water to remove them. The rate at which individual constituents are removed relative to their abundance in the rocks—their “relative mobility”—however, is notably different. The relative abundance of individual elements in the rock and in the water offers a means of determining the relative mobility (Smyth, 1913, called it relative solubility) of the common elements. These determinations, in turn, provide some insight into the rates at which individual minerals yield to weathering and to the fate of the weathering products, designating products that are carried away from sites of weathering in the water and those that remain in place.

Calculations of the relative mobility of the elements in weathering suggest that the order of mobility in the Sierra Nevada granitic terrane is $Ca \geq Na > Mg > Si \geq K$. Aluminum and iron are of nearly equivalent mobility with one another but are much less mobile than the other five elements considered. This sequence accords in general with calculations of Smyth (1913), Polynov (1937, p. 162), and Miller (1961), but differs from calculations by Anderson and Hawkes (1958), in whose sequence magnesium is placed first and the other elements conform to the order shown above.

All these authors made their estimates using the mineral composition of surface water. Smyth based his calculations on an assumed average chemical composition of the rocks at the surface of the earth and on an estimate for the average composition of river water of the earth.

Polynov used an average composition for igneous rock and an average composition for water draining igneous-rock terrane. Anderson and Hawkes, Miller, and the work here reported restrict the study to specific rock terranes and to water emerging from them, but only in the present study were all samples from ground water. The close similarity in results emerging from such diverse points of approach suggests that the relative mobility determined for the elements represents a geochemical phenomenon having broad application. The differences caused by consideration of mobility in restricted environments is equally significant as a variable to be considered when specific geochemical relations are studied.

STANDARD PROCEDURE

The usual procedure followed is that proposed by Smyth (1913). For each element considered, the percentage in the rock is divided into the equivalent percentage in water draining from the rock. The greater the resulting ratio, the greater the assumed mobility of the element. For each sample, the weight percentages of the elements considered are recalculated (normalized) so that the total for the rock and for the water will each be 100 percent.

The mean composition of the granitic rocks in the Sierra Nevada was calculated from data given by Bateman (1961, p. 1525) by weighting the average values as follows: Quartz diorite, 1; granodiorite, 5; and quartz monzonite, 7. Not only was this weighting procedure in accordance with the number of samples reported by Bateman, but, more significantly, it was the opinion of the present writers that the weighting used approximates the relative abundances of the several rock types in the terranes drained by the springs sampled. The results, recalculated to 100 percent, are compared in table 6 with equivalent data from the ephemeral and perennial springs, also recalculated to 100 percent. The ratio $\frac{\text{percentage of element in water}}{\text{percentage of element in rock}}$ expresses

the relative mobility of the seven elements in the same terms used by Smyth and the others. The results— $\text{Ca} \geq \text{Na} > \text{Mg} > \text{Si} \geq \text{K} > \text{Fe} \geq \text{Al}$ —conform essentially to Smyth's, Polynov's, and Miller's conclusions but differ from those of Anderson and Hawkes.

If the 18 springs assigned to the quartz monzonite group and the 18 assigned to the granodiorite group (table 1) are related to the average composition of quartz monzonite and granodiorite (Bateman, 1961, p. 1525), respectively, the results are as shown in table 7. For quartz monzonite and springs related to quartz monzonite, the apparent relative mobility is $\text{Ca} > \text{Mg} > \text{Na} > \text{Si} = \text{K} > \text{Fe} > \text{Al}$. In the calculations for granodiorite and for springs related to that rock, however, the sequence determined is $\text{Na} > \text{Ca} > \text{Mg} > \text{K} > \text{Si} > \text{Fe} > \text{Al}$.

TABLE 6.—Relative mobility of common elements determined from weight-percentage composition of average rock and of average water from springs (recalculated to 100 percent)

Element and source	Perennial springs		Ephemeral springs	
	Percent	Ratio W/R	Percent	Ratio W/R
Si { Water.....	38. 89	} 0. 63	48. 15	} 0. 78
Si { Rock.....	61. 53		61. 53	
Al { Water.....	. 05	} . 003	. 18	} . 01
Al { Rock.....	15. 77		15. 77	
Fe { Water.....	. 12	} . 024	. 36	} . 07
Fe { Rock.....	5. 07		5. 07	
Ca { Water.....	31. 32	} 7. 08	19. 13	} 4. 33
Ca { Rock.....	4. 42		4. 42	
Mg { Water.....	4. 89	} 2. 88	3. 83	} 2. 25
Mg { Rock.....	1. 70		1. 70	
Na { Water.....	19. 33	} 3. 89	21. 38	} 4. 30
Na { Rock.....	4. 97		4. 97	
K { Water.....	5. 38	} . 82	6. 98	} 1. 07
K { Rock.....	6. 53		6. 53	
Relative mobility: Ca > Na > Mg > K > Si > Fe > Al			Ca = Na > Mg > K > Si > Fe > Al	

RELEASE AND RETENTION OF ELEMENTS

There is great consistency in the behavior of silica, potassium, aluminum, and iron. Their percentage abundance is far greater in the rocks than in the water that drains from the rocks. The aluminum and iron are especially conspicuous in this respect. Some of the aluminum released by weathering of the rock-forming minerals is utilized in the formation of clay minerals. An equal or greater part is probably immobilized by formation of hydrated aluminum oxides. The relative immobility of the iron is perhaps explained entirely by formation of hydrated oxides that, like those of aluminum, are virtually insoluble at conditions of pH and Eh prevailing at the sites of weathering. The formation of clay minerals may also tend to immobilize silica and potassium: the silica is a constituent part of the clay molecule, and the lesser amounts of potassium are retained

TABLE 7.—Relative mobility of common elements calculated from their concentrations in water from springs and their abundances in rocks, considered by groups (re-calculated to 100 percent)

Element and source	Quartz monzonite and quartz monzonite related springs		Granodiorite and granodiorite related springs		
	Percent	Ratio W/R	Percent	Ratio W/R	
Si {	Water-----	43. 78	} 0. 69	45. 30	} 0. 79
	Rock-----	65. 99		57. 38	
Al {	Water-----	. 0006	} . 00003	. 0005	} . 00003
	Rock-----	15. 32		15. 93	
Fe {	Water-----	. 001	} . 0004	. 0007	} . 00009
	Rock-----	2. 75		7. 29	
Ca {	Water-----	29. 19	} 11. 45	24. 51	} 3. 99
	Rock-----	(?)		6. 14	
Mg {	Water-----	4. 03	} 6. 83	3. 60	} 1. 25
	Rock-----	. 59		2. 88	
Na {	Water-----	17. 56	} 3. 44	21. 15	} 4. 41
	Rock-----	5. 11		4. 80	
K {	Water-----	5. 22	} . 68	5. 29	} . 95
	Rock-----	7. 66		5. 56	
Relative mobility: Ca > Mg > Na > Si = K > Fe > Al			Relative mobility: Na > Ca > Mg > K > Si > Fe > Al		

by sorption. Utilization of potassium by vegetation may also contribute to the element's low mobility.

The smaller relative mobility of calcium and magnesium in the environment of the ephemeral springs than in the environment of perennial springs implies selective removal of sodium where the activity of the hydrogen ion is high. The median pH of the ephemeral-spring water (table 2) is lower than that of the perennial springs. As hydrogen-ion activity lessens and pH rises, the rate of removal of sodium from mineral molecules seems to decrease. In turn, the percentage of the alkaline earths in water increases, and their apparent relative mobility likewise rises. That sodium is the most mobile of the elements in waters from granodiorite is unexpected. Granodiorite should contain more calcium in the plagioclase feldspar and in hornblende than does quartz monzonite. Calcium should, therefore,

be more available to water in contact with granodiorite—sodium, if anything, should be less available. There is no ready explanation for this apparent anomaly unless the sodium is derived from minerals other than feldspar, such as sodic amphiboles. Presence of the latter minerals has not, however, been determined in granodiorite from the study area.

COMPARISONS WITH WATER FROM OTHER SOURCES

Comparison of the chemical character of water from ephemeral and perennial springs with that of water from other sources shows that:

1. Water in small streams of the Sierra Nevada, sampled long after snowmelt runoff has ceased—the base flow—is notably similar in type and concentration to water from the ephemeral springs.
2. Water from thermal springs rising from granitic rock in the Sierra Nevada has considerably more dissolved solids than does water from the nonthermal perennial springs; the thermal water is of sodium mixed-anion type and is commonly at or near saturation with respect to calcite.
3. Water from granitic rocks in different climatic environments is commonly of markedly different chemical type from that in the Sierra Nevada.
4. Water from perennial springs in volcanic rocks in the Sierra Nevada and southern Cascade Mountains is somewhat higher in mineral content and magnesium percentage than is water from the perennial springs in granitic rock, but it is in other respects much like the water from springs in granitic rock.
5. By inference, the atmosphere and lithosphere interact to control the chemical character of natural water. In any one climatic environment the effect of the lithosphere can locally be recognized. Where the climatic environment imposes extreme conditions, as in the desert or on a seacoast, it may mask the effect of the lithosphere on chemical water types.

STREAM WATER

The water flowing in small streams in the Sierra Nevada is notably similar to that of the ephemeral springs in chemical type and in concentration of dissolved solids. This is especially true of samples taken long after snowmelt runoff had ceased—when the streams were supported by their base flow. Comparison of mean concentrations (table 8) shows that the base flow and water of the ephemeral sources show relations close to unity (col. G, table 8) except for sulfate, chloride, and nitrate. These three are increased in concentration in the stream water by factors of 2.0, 2.6, and 10, respectively. During snowmelt runoff, stream water on the average contains somewhat less dissolved solids than does water from ephemeral springs (cols. C, E, table 8).

The close resemblances noted further emphasize the rapidity with which mineralization is attained by melting snow after it contacts the lithosphere. The greater concentrations of chloride, sulfate,

TABLE 8.—Comparisons of mean concentrations in parts per million of major constituents in ground and surface water

Constituent	(A)	(B)	(C)	(D)	(E)	(F)	(G)
	Ephemeral springs	Perennial springs	Streams (snowmelt runoff)	Streams (base flow)	$\frac{C}{A}$	$\frac{D}{B}$	$\frac{D}{A}$
Silica (SiO ₂)	16	25	8.1	12	0.5	0.5	0.8
Calcium (Ca)	3.1	10	2.4	4.4	.8	.4	1.4
Magnesium (Mg)	.7	1.7	.6	.9	.9	.5	1.3
Sodium (Na)	3.0	6.0	1.5	2.7	.5	.4	.9
Potassium (K)	1.1	1.6	.7	1.0	.6	.6	.9
Bicarbonate (HCO ₃)	20	57	14	21	.7	.4	1.0
Sulfate (SO ₄)	1.0	2.4	1.3	2.0	1.3	.8	2.0
Chloride (Cl)	.5	1.1	.4	1.3	.8	1.2	2.6
Fluoride (F)	.07	.09	.04	.07	.6	.8	1.0
Nitrate (NO ₃)	.02	.3	.1	.2	5.0	.7	10
Dissolved solids (calculated)	36	75	22	35	.6	.5	1.0

and nitrate in the stream water are not explained by existing information. The difference in median pH—7.0 in the stream water, 6.2 in that from ephemeral springs—presumably reflects a trend toward equilibration with the carbon dioxide of the atmosphere.

THERMAL SPRINGS

Water from eight thermal springs rising from granitic rock in the Sierra Nevada (pl. 1) is of sodium mixed-anion type, being notably higher in percentage content of sulfate and chloride than is water from the nonthermal springs. In six of the eight thermal-spring samples, the pH exceeds 8.0; on the basis of calculations suggested by Garrels (1960, p. 52–54), water from these six springs is at or near saturation with respect to calcite. The data for dolomite are less complete, but on the basis of a solubility product for dolomite of $10^{-19.33}$ (Garrels, Thompson, and Siever, 1960, p. 412), calculations suggest that the solubility of dolomite is also exceeded.

The relatively high pH, therefore, seems to control the small amounts of the alkaline earth metals found in the thermal-water samples. Chemical analyses of the water (table 9) and a graph (fig. 11) show the essential relations.

With the foregoing in mind, the chemical quality of the thermal water can largely be explained (D. E. White, 1957; oral communication, 1962) as the result of deep circulation of meteoric water. At the somewhat elevated temperatures attained during deep circulation, the chemical aggressiveness of the water is increased and the H⁺ ion content is exhausted by vigorous hydrolysis of silicate minerals, thus raising pH to the levels observed. The sodium content continues to increase as H⁺ ions displace cations from the silicate frame-

TABLE 9.—Chemical analyses of water from thermal springs

Spring and analysis number	Bowers Mansion Warm Spring, Nev. 1136	Walley Hot Spring, Nev. 1156	California Hot Spring 1214	Warm Spring near Meyers, Calif. 1219	Grovers Hot Springs, Calif. 1253	Seovern Hot Springs, Calif. 1299	Unnamed Spring near Calpine, Calif. 1563	Arnold Spring, Calif. 1578
Temperature (°C).....	49	60	50	24	65	56	20	18
Silica (SiO ₂).....	45	61	54	22	96	65	28	36
Calcium (Ca).....	3.2	9.6	1.6	2.8	34	2.8	3.6	46
Magnesium (Mg).....	1.0	.5	.2	.0	2.2	.2	.1	3.3
Strontium (Sr).....			.04		3.7	.15	.00	.25
Sodium (Na).....	45	137	59	33	428	136	77	64
Potassium (K).....	.6	2.9	.4	.9	11	2.7	.8	1.8
Lithium (Li).....	.11	.19	.06	.02	.81	.22		
Bicarbonate (HCO ₃) ¹	70	40	82	37	760	268	47	150
Carbonate (CO ₃) ¹	6.0	2.7	7.2	4.8	0	2.5	5.2	0
Hydroxide (OH) ¹3	.2	.3	.4	0	0	.3	0
Sulfate (SO ₄).....	36	200	6.0	13	160	17	33	9.2
Chloride (Cl).....	4.0	46	28	14	183	37	59	102
Fluoride (F).....	3.4	5.0	2.0	.5	4.2	8.5	.8	.6
Nitrate (NO ₃).....	.0	.3	.0	.0	1.3	.0	.0	.2
Orthophosphate (PO ₄).....	.06	.06	.06	.06	.5	.01		
Boron (B).....	.21		.49	.25	2.4	2.5		
Dissolved solids (calculated).....	180	492	207	114	1,300	409	238	335
pH (field).....	9.2	9.0	9.2	9.4	7.0	8.2	9.3	7.5

¹ Where pH>7.5, values for HCO₃, CO₃, and OH were obtained using equilibrium equations and the stoichiometric relations of the ions in the alkalinity determination corrected for dissociated silicic acid.

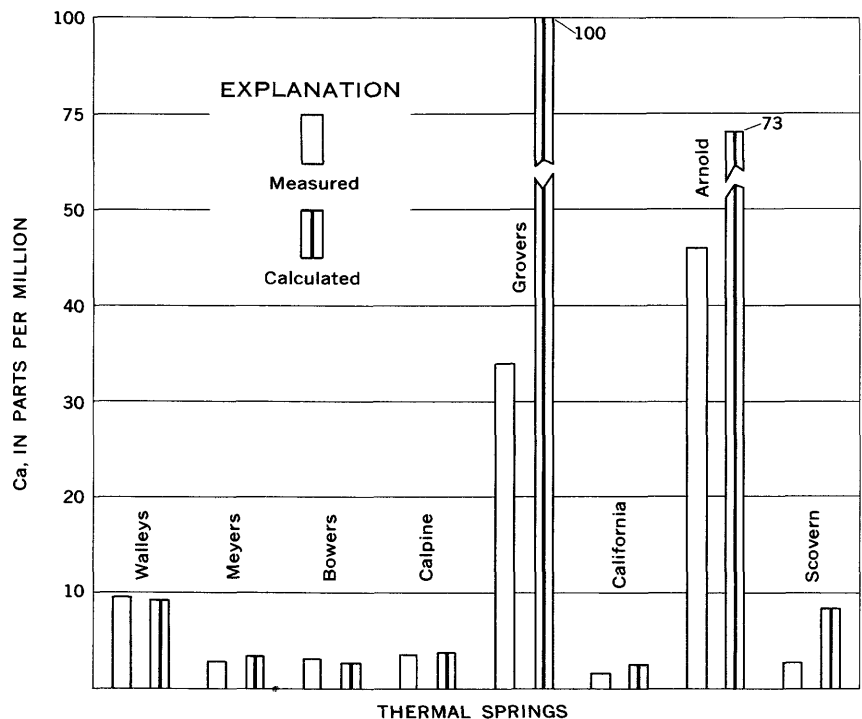


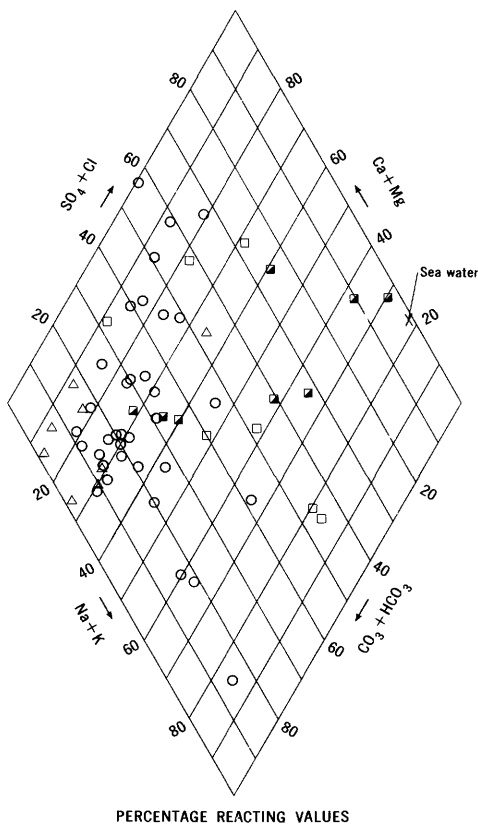
FIGURE 11.—Graph showing calculated and measured calcium content in water from eight thermal springs (listed in table 9).

work; calcium is removed by precipitation; and chloride and fluoride contents increase as the result of attack by the water on minerals containing these halides either in fluid inclusions or as replacements of elements in the lattices of minerals such as biotite. Magnesium may be held at low levels of concentration by equilibrium relations with dolomite; or, together with potassium, it may be incorporated in the clay minerals formed during alteration of the igneous rocks. Chloride contents (analyses 1253 and 1578, table 9) of more than 100 ppm, sulfate contents (analyses 1156 and 1253, table 9) greater than 150 ppm, and bicarbonate contents (analyses 1253 and 1299, table 9) of 760 ppm and 268 ppm, respectively, remain unexplained by the foregoing hypotheses. These concentrations imply addition of nonmeteoric water to the systems, the sources of the additions remaining undiscovered. But, on the basis of present geochemical knowledge, the overall pattern of events can best be envisioned as outlined above.

EFFECTS OF THE CLIMATIC ENVIRONMENT ON GROUND WATER FROM GRANITIC ROCKS

Water from seven springs in granitic rock of the Idaho batholith (J. D. Hem, written communication, 1959) is closely analogous (fig. 12) to Sierran granitic water in overall chemical character. Calcium and magnesium make up a greater percentage of the cations in the water from Idaho than from the Sierra, and the overall mineral content is somewhat greater. Water from 36 wells in granitic terrane of North Carolina (Billingsley, Fish, and Schopf, 1957; Fish, LeGrand, and Billingsley 1957) is appreciably higher in mineral content than is water from the Sierra Nevada; although diverse in chemical character (fig. 12), the water from North Carolina is generally a calcium magnesium bicarbonate type. The diversity in type shown by samples from North Carolina may result in large part from the grouping of water as "from granite" where in fact the samples came from a variety of aquifers ranging in composition from granite to diorite, mica schist, and granite gneiss, according to the authors cited above.

Water from seven springs in the Mojave Desert (Thompson, 1929) shows considerable diversity in type (fig. 12) and shows about 6 times the mineral content of the average Sierra Nevada perennial-spring water. Water from eight springs in granitic coastal areas of California, analyzed in the present study, is partly of calcium magnesium bicarbonate type (fig. 12), partly of sodium chloride type, and partly mixed in character. The coastal water has, on the average, more than 1½ times the dissolved-solids content of water in the Sierra Nevada springs.



EXPLANATION

Source	Number of samples	Dissolved-solids content, in parts per million			
		Max	Median	Min	Mean
□ Springs—Mojave Desert	7	860	583	334	579
■ Springs—California coast	8	242	128	51	134
△ Springs—Idaho batholith	8	154	89	73	100
○ Wells—North Carolina	36	417	120	54	141

FIGURE 12.—Diagram showing general chemical character both of water from granitic rock in four different environments and of sea water.

Although a detailed breakdown of the processes involved in the differentiation of chemical types observed cannot be made with existing information, a few general conclusions are warranted. Work in the Sierra Nevada showed that the granitic rocks, as a group, yield water of closely comparable chemical quality regardless of the mineralogical differences in the source rocks. The behavior of minerals in the soil—under prevailing climatic conditions—is thought to be largely responsible for the mineral content observed in the water. Chemical and mineralogical differences unquestionably exist among granitic rocks in the several areas, and some of the variation in chemical character of the water no doubt is caused by those differences.

Spring water from granitic terranes in the Mojave Desert of southern California is fairly highly mineralized as a result of concentration by evaporation and as a result of the addition of chloride and sulfate by solution of saline dust derived locally from playa areas and from more ancient deposits of saline minerals that abound in the Mojave. Fault-zone water, which contains much sulfate and chloride, may also contribute to the reported mineralization. Detailed chemical analyses, including determinations of characteristic desert-dust constituents such as boron and strontium, and analyses of samples of precipitation, have not been made. They would help to determine the controls that cause the observed chemical character of the desert-spring water.

The controls having the greater effect on the chemical character of the water, however, are probably climatic rather than mineralogical. The water analyses shown in figure 12 that most nearly resemble those of water from the perennial springs of the Sierra Nevada in type and concentration are those from Idaho. Precipitation over the area of the batholith in Idaho is as great as, or greater than, that over the Sierra Nevada; but runoff (fig. 1) is less, which implies a higher rate of evaporation, greater use by vegetation, or both, in Idaho. These processes and small differences in mineralogy seem to explain adequately the observed differences between the water from the two areas.

Well water from North Carolina is probably more appreciably influenced by mineralogical differences in the several rock types that make up the aquifers sampled. In addition, the eastern seaboard has precipitation distributed throughout the year whereas in the Sierra Nevada, as shown earlier, precipitation is sparse and irregular except in winter. The result is deeper and more complete weathering of the rock and formation of more mature soils under a heavier cover of vegetation on the eastern seaboard than is common in the Sierra Nevada. Also, the eastern seaboard receives precipitation seasonally from storms originating over the ocean. These storms undoubtedly carry oceanic constituents, especially chloride, into the area.

Water from springs in granitic rocks along the California coast shows the predominant influence of salts blown inland from the ocean. Two samples, (fig. 12) both from Point Reyes Peninsula, have chemical compositions notably close to the composition of sea water, although the concentrations of individual elements are much smaller. Other samples, some from Point Reyes and some from farther south near Monterey, are less influenced by the nearby ocean. Plots of three samples (fig. 12) are in the field occupied by plots of samples from the North Carolina wells, but none are within fields occupied by plots of samples from perennial springs in the Sierra Nevada or Idaho batholiths. These relations and the higher average mineralization of the coastal water imply that along the California coast there is more active weathering of the rock and deeper soil formation than is characteristic inland. Certainly the vegetation is more abundant along the coast than in the Sierra Nevada. Considering the significance of the soil as a source of dissolved solids, it is likely that the character of the coastal water is determined by proximity to the sea and by the more active weathering of the rock in that area.

WATER FROM VOLCANIC ROCKS

Water from 25 perennial springs in volcanic terrane of the Sierra Nevada and southern Cascade Mountains differs from the water from granitic-terrane springs primarily by having $1\frac{1}{2}$ times the mineral content, on the average, and by having a significantly higher percentage of magnesium (table 10; table 2). The mean content of dissolved solids in the granitic spring water is 75 ppm; that in the volcanic-rock springs is 126 ppm. Similarly, in the granitic spring water magnesium averages 12 percent of the cations; it is nearly 31 percent in water from volcanic rock. Studied using the *t* test, the difference observed has significance greatly exceeding the 0.01 level. The differences in calcium percentage are not statistically significant, but the differences in percentages of sodium are significant at a level of 0.03, and differences in potassium, at 0.05. The bicarbonate percentage among the anions is even greater in water from volcanic rock than in water from granitic rock, and the sulfate and chloride percentages are correspondingly smaller in the volcanic-rock water.

The average strontium content in the volcanic-rock water is somewhat larger than that in the water from granitic rock. The overlap of absolute and percentage concentrations of strontium, however, makes it unfeasible to use strontium content to differentiate water from the two rock types. The greater content of magnesium in volcanic-rock water is caused presumably by the larger proportion of magnesium in the minerals composing the volcanic rock. The greater mineralization of the volcanic-rock water no doubt results from the

TABLE 10.—Concentrations of major constituents in water from springs in volcanic terrane

[Data in parts per million except pH]

Constituents or property	Volcanic springs (25 samples except as noted)			
	Maximum	Median	Minimum	Mean
SiO ₂ -----	62	40	24	40.6
Al ¹ -----	.25	.015	.00	.04
Fe ¹ -----	.05	.01	.00	.015
Ca-----	34	14	4.0	15.32
Mg-----	13	6.6	1.0	6.63
Sr ² -----	.38	.025	.04	-----
Na-----	16	8.0	3.2	8.41
K-----	5.1	1.8	.3	2.12
HCO ₃ -----	172	100	32	99
SO ₄ -----	16	.8	.0	2.26
Cl-----	3.6	1.7	.3	1.60
F ³ -----	.1	.1	.0	.07
NO ₃ -----	2.2	.2	.0	.60
Sum of dissolved solids	215	128	70	126
pH (lab.)-----	7.6	7.0	6.1	-----

	Percentage composition		
	Maximum	Mean	Minimum
SiO ₂ -----			
Sum of dissolved solids (ppm)-----	63	33.8	16
Ca-----			
Cations (epm)-----	54	44.6	31
Mg-----			
Cations (epm)-----	48	30.8	17
Na-----			
Cations (epm)-----	30	21.1	11
K-----			
Cations (epm)-----	10	3.3	1
HCO ₃ -----			
Anions (epm)-----	99	94.9	87
SO ₄ -----			
Anions (epm)-----	10	2.2	0
Cl-----			
Anions (epm)-----	5	2.6	<1

¹ 10 samples.

² 22 samples.

³ 11 samples.

presence, and generally ready solubility, of volcanic glass in the less completely crystallized lavas and tuffs.

The similarities among samples of water from granitic and volcanic rocks in the Sierra Nevada and southern Cascade Mountains, and

water from granitic rocks in Idaho, reflect similarities in climate as well as similarities in the rock content of a small number of minerals that largely govern the chemical type of water. The observed differences reflect partly climate and mineralogy. The two cannot always be segregated. The differences between water from granitic rocks in the Sierra Nevada on the one hand and from the rocks of the Mojave Desert and California coast on the other imply dominance of the climatic environment as the control over water quality in those areas.

STABILITY RELATIONS

Another approach to the understanding of water from granitic terrane is through the use of stability diagrams compiled from thermochemical data. The results of the following study indicate that the chemical characteristics of the water in the Sierra Nevada are such that kaolinite is a stable weathering product whereas potassium-mica and montmorillonite are unstable.

Only recently have thermochemical data for aluminosilicate minerals been obtained at low temperature and pressure in the laboratory. This delay is due primarily to the low solubility of these minerals at such temperatures and pressures and to difficulties in determining heats of solution of the alkali oxides and alumina using the techniques of calorimetry.

The thermochemical data for the minerals of significance are not only limited, but the several authors have reported conflicting values for individual reactions. However, enough information is available for stability relations to be of value. The data used in constructing the stability diagrams, as well as the source from which the data were obtained, are listed in table 11.

TABLE 11.—Standard free energies of formation of compounds and ions at 25°C and 1 atmosphere total pressure

[Modified from Garrels (1960)¹]

Formula	Description	State	ΔF_f° (kcal)
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Gibbsite.....	Crystalline.....	-554. 6
$\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$	Kaolinite.....	do.....	-895. 1
H^{+1}		Aqueous.....	0
KAlSi_3O_8	Potassium feldspar.....	Crystalline.....	-871. 6
$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	Mica.....	do.....	-1316. 2
K^{+1}		Aqueous.....	-67. 46
$\text{NaAlSi}_3\text{O}_8$	Albite.....	Crystalline.....	² -868. 9
Na^{+1}		Aqueous.....	-62. 59
H_2O	Water.....	Liquid.....	-56. 7
OH^{-1}		Aqueous.....	-37. 60
H_4SiO_4	Silicic acid.....	do.....	-305. 6

¹ The standard free energies have been adjusted on basis of ΔF_f° quartz = 197.3 kcal for the compounds containing silica.

² Calculated from heat of formation from the oxides as determined by Kraeck (1953).

The two principal stability diagrams are those which involve the phases in the systems $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. The stability diagrams were constructed using the equilibrium constant for a particular reaction calculated from the free energy of formation of the constituents involved in the reaction. For example:



$$\Delta F_{\mathbf{R}}^{\circ} = c\Delta F_{fC}^{\circ} + d\Delta F_{fD}^{\circ} - a\Delta F_{fA}^{\circ} - b\Delta F_{fB}^{\circ} \quad (5)$$

where

$\Delta F_{\mathbf{R}}^{\circ}$ = standard free energy of the reaction

ΔF_{fA}° , ΔF_{fB}° , ΔF_{fD}° , ΔF_{fC}° = standard free energies of formation of the reactants and products.

Also

$$\Delta F_{\mathbf{R}}^{\circ} = RT/n \text{ keq} \quad (6)$$

Where

R = gas constant

T = absolute temperature

keq = equilibrium constant

$$\text{keq} = \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (7)$$

Where

a_C , a_D , a_A , a_B = activities of products and reactants.

The assumptions are made that the activity of any solid is unity and that the molality of soluble constituents equals activity. The granitic waters have low concentrations of dissolved solids, and values for the free energy of formation of the constituents are not known with a high degree of certainty; therefore these assumptions seem justified.

The free energies of formation are based on a temperature of 25°C. The analyzed waters had orifice temperatures that ranged from 5°C to 22°C. The error due to deviation of temperature from 25°C is within the accuracy of the other data.

From these equations, the stability relations can be written as functions of $\frac{[\text{K}^{+1}]}{[\text{H}^{+1}]}$ and $[\text{H}_4\text{SiO}_4]$. The construction of the stability relations as functions of $\frac{[\text{K}^{+1}]}{[\text{H}^{+1}]}$ is based on a stability diagram obtained from R. M. Garrels (written communication, 1961). The results given in figure 13 suggest that these granitic waters fall within the stability field of the kaolinite phase.

For the system, $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, the phases considered are given in the following equations. These equations were used to determine the field of stability of the different phases.

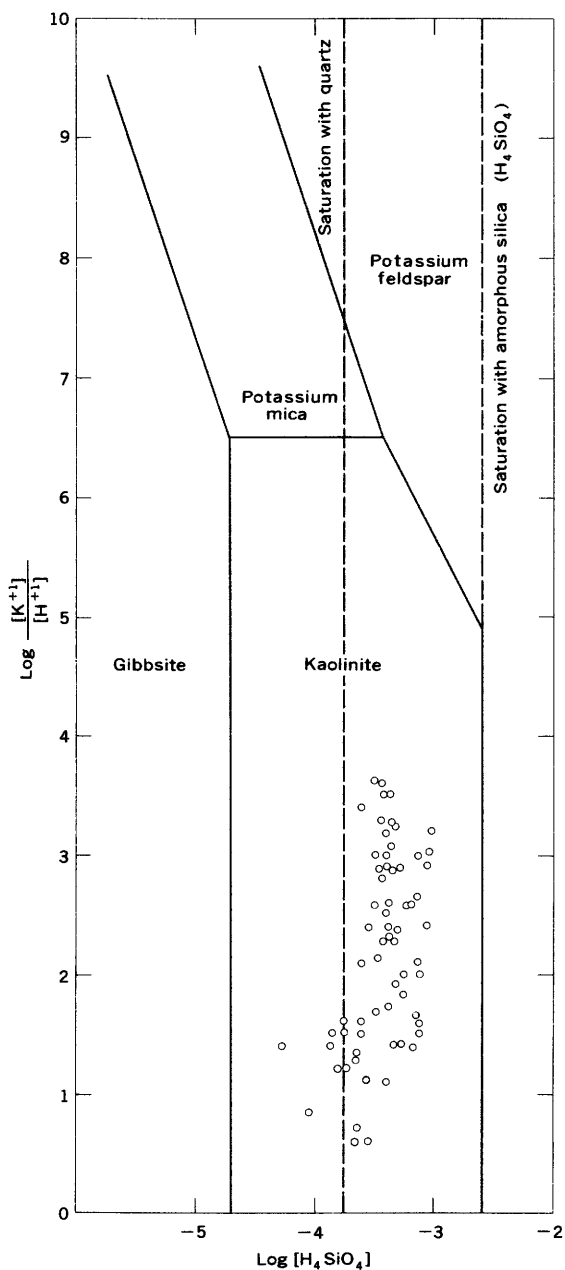
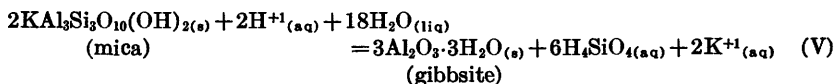
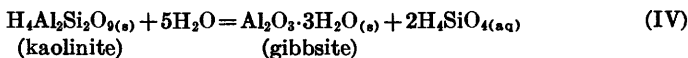
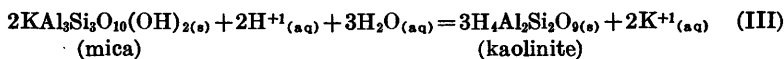
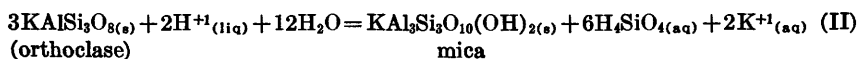
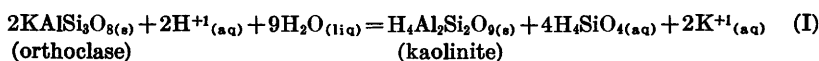
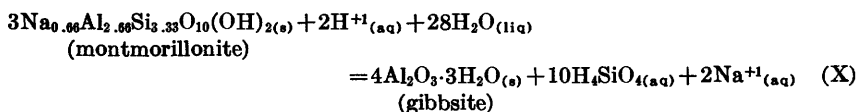
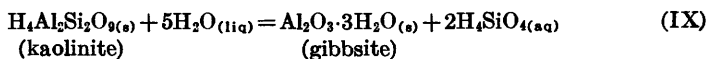
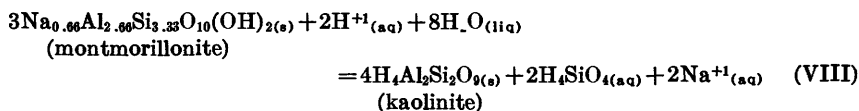
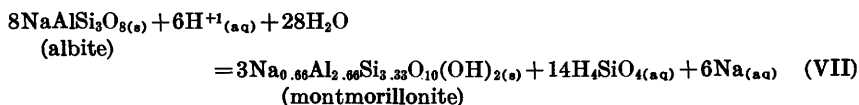
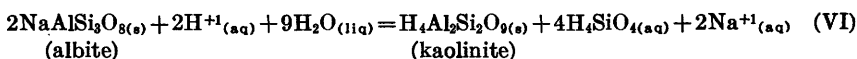


FIGURE 13.—Stability relations of phases in the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C and 1 atmosphere total pressure as functions of $[\text{K}^{+1}]/[\text{H}^{+1}]$ and $[\text{H}_4\text{SiO}_4]$.



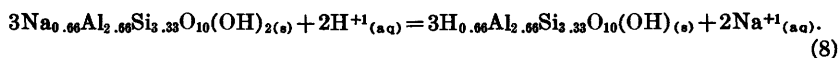
Similarly, in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, the field of stability of the different phases can be determined from the following equations:



The stability relations can be written as a function of $\frac{[\text{Na}^+]}{[\text{H}^+]}$ and $[\text{H}_4\text{SiO}_4]$.

The equilibrium constant for montmorillonite in equilibrium with kaolinite (equation VIII) was estimated from the titration curves of hydrogen-montmorillonite by Marshall (1949, p. 109) and from the alteration reaction of montmorillonite to kaolinite determined by Hemley and others (1961, p. D338).

Although the exact composition of the montmorillonite is not known, a reaction for the titration of a hydrogen-montmorillonite may be written as follows:

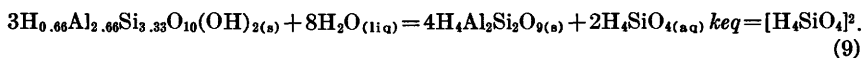


The equilibrium constant for this reaction is $keq = \frac{[Na^{+1}]^2}{[H^{+1}]^2}$.

From the titration curves by Marshall (1949, p. 109) keq is estimated as approximately 10^{10} .

From equation 6, ΔF_R° is calculated as -14 kcal.

Also, according to the following reaction,

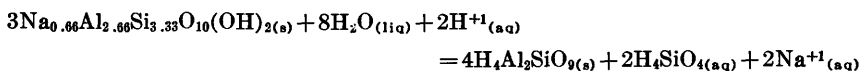


Hemley and others (1961, p. D338) found that when montmorillonite is altered to kaolinite, the silica phase crystallizes into cristobalite. This suggests that the concentration of silica at equilibrium is equal to the solubility of cristobalite.

Thus, if the above is assumed to be true, then the silicic acid concentration at equilibrium for the reaction (equation 9) is estimated as approximately $10^{-3.1}$ (solubility of cristobalite at $25^\circ C$). Therefore, keq of equation 9 = $10^{-6.2}$.

Thus ΔF_R° is calculated to be $+8.5$ kcal.

The addition of equations 8 and 9 results in equation VIII



where

$$\Delta F_R^\circ(v_{III}) = -5.5 \text{ kcal.}$$

From equation 6, $keq = 10^{+4}$.

Equation VIII can be obtained by subtracting equation VII from four times equation VI. Therefore

$$\Delta F_R^\circ v_{III} = 4\Delta F_R^\circ v_I - \Delta F_R^\circ v_{VII}$$

The equilibrium constant for equation VII can then be calculated from equation 6. The same procedure was used to estimate the equilibrium constant for equation X. In this instance, equations VIII and IX were involved in the calculation.

A plot using data obtained by analyses of waters from granitic-terrane springs and seeps as a function of $\frac{[Na^{+1}]}{[H^{+1}]}$ and $[H_4SiO_4]$ is given in figure 14. All waters fall in the field of stability of kaolinite as functions of $\frac{[Na^{+1}]}{[H^{+1}]}$ and $[H_4SiO_4]$.

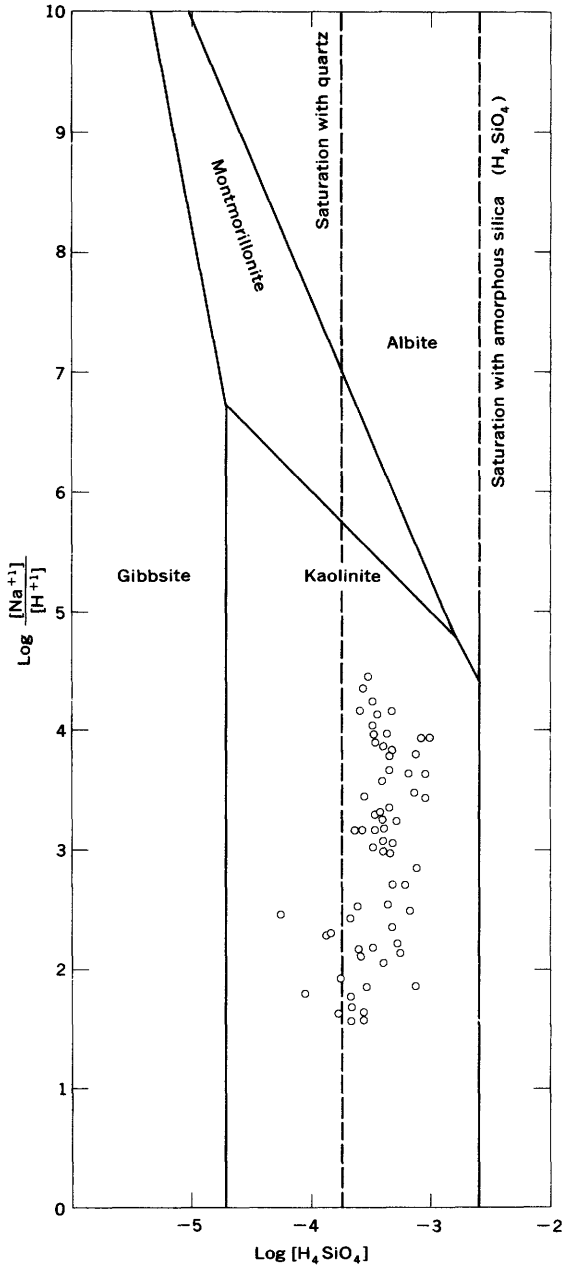


FIGURE 14.—Stability relations of phases in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C and 1 atmosphere total pressure as functions of $[\text{Na}^{+1}]/[\text{H}^{+1}]$ and $[\text{H}_4\text{SiO}_4]$.

Both stability diagrams suggest that potassium-mica and montmorillonite are unstable. However, mica and montmorillonite were identified in some locations. Their presence probably means that the $\frac{[Na^{+1}]}{[H^{+1}]}$ and $\frac{[K^{+1}]}{[H^{+1}]}$ ratios and (or) the silicic acid concentration would have to change until an equilibrium is approached between kaolinite and these clay minerals or else these clay minerals would eventually dissolve or be converted into some other product.

Figure 14 shows that the upper limit of silica is approximately $10^{-3.0}$ moles per liter. The solubility of cristobalite at $25^{\circ}C$ is about $10^{-3.1}$ moles per liter of silicic acid. This suggests that the upper limit of the silicic acid concentration may be controlled by the solubility of cristobalite. That the higher $\log \frac{Na^{+1}}{H^{+1}}$ ratios are approaching the montmorillonite-kaolinite boundary and that the silicic acid concentration does not exceed the solubility of cristobalite suggest that some of the chemical constituents of these waters may be controlled by a montmorillonite-kaolinite equilibrium.

It should be emphasized that the stability diagrams, figures 13 and 14, only represent pure hydrous alkali aluminosilicate systems and that they do not take into consideration variation in composition of the minerals which occur in nature. However, such diagrams are useful in obtaining a general picture of what may be occurring in nature.

CONCLUSIONS

The mineral content of ground water in granitic terrane in the Sierra Nevada comes from precipitation and from the lithosphere. About 95 percent of the total mineral content is derived from the lithosphere, including the soil and its contained gases. Of this 95 percent, approximately half is acquired during the first few hours to few weeks of contact between melting snow and soil and saprolite; silica makes up a large part of the early mineral increment.

All the metallic constituents commonly found in water, plus silica, are available in the rock and its weathering products in abundances greater than the capacity of percolating water to remove them. The aggressiveness with which water attacks the minerals in soil and solid rock is a direct function of the hydrogen-ion content of the water. In the Sierra Nevada water the hydrogen-ion content is controlled almost exclusively by solution of carbon dioxide derived from the soil atmosphere. The alkalies, sodium and potassium, are preferentially released from the mineral lattices when the hydrogen-ion content is high; as reactions between rock and water continue and hydrogen-ion content is correspondingly reduced, the system approaches equilibrium

and further release of alkalis from the minerals is progressively reduced. There is no detected limit to the degree to which calcium and magnesium may be removed from the minerals other than total hydrogen-ion content.

Aluminum and iron are virtually immobilized at sites of weathering by formation of hydrous oxides that resist solution by water. Potassium is partly immobilized by the combined processes of adsorption by clay minerals and utilization by plants. Magnesium may be partly immobilized by adsorption. Silica is available in such great abundance that, despite its presence in large amounts in the water, much of the total amount released by weathering remains in place either as a component of weathering products such as clay minerals or in noncrystalline form.

The water from granitic rocks in the Sierra Nevada is thermodynamically stable with respect to kaolinite, according to estimated equilibrium relations. X-ray diffraction studies show the presence of kaolinite, montmorillonite, and mica in some places and the common presence of poorly crystallized clay minerals. These relations imply a system in which weathering products are trending toward formation of kaolinite, although in many localities the kaolinite could not be identified.

Part of the small amount of sulfate and chloride available from precipitation and from weathering of the rock minerals is apparently removed from solution. Kaolinitic clay and the hydrous oxides of iron reportedly have the capacity to adsorb these anions where pH is less than about 7.0. Under these conditions, and where water has small contents of chloride, the usefulness of chloride as a geochemical tracer is open to question.

In the Sierra Nevada and in other areas that are underlain by igneous rocks of varying lithology and that have a comparable continental climate, the water is likely to be a mixed-cation bicarbonate type having a total mineral content ranging from about 25 to 200 ppm but averaging between 75 and 150 ppm. Where climatic environments are materially different, as in desert or seaboard areas, the mineral content is likely to be two to five times larger, and the percentages of sodium, sulfate, and chloride may be very much larger.

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