

Geochemical Evidence On The Nature Of The Basement Rocks Of The Sierra Nevada, California

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By Ivan Barnes, R. W. Kistler, R. H. Mariner and T. S. Presser

Abstract

CO₂-rich waters from 17 soda springs of the Sierra Nevada have been analyzed. Ten of these waters have high concentrations of magnesium and are saturated with amorphous silica at the temperature (near mean annual air temperature) of the springs. This combination of high magnesium concentrations, amorphous silica saturation, and low temperature is unique to the phase assemblage serpentine-water-carbon dioxide, and it requires either an isothermal gradient in the ground water and adjacent rocks or shallow depth to the serpentine. Magnesium concentrations in the Sierra spring waters are lower than those found in carbonate spring water under similar physical and chemical conditions in lizardite-chrysotile serpentine terranes; therefore the serpentinites under the Sierra Nevada may be antigorite. Soda springs in the Sierra Nevada have calcium concentrations in the range of 120 to 620 mg/L, probably from calcite-bearing rocks that are being dissolved by the water. Isotopic compositions of strontium in the water from some of the springs are consistent with the calcite being of Middle Devonian to early Mesozoic age. Strontium in CO₂-rich waters issuing from metamorphic rocks containing biotite and muscovite yields much higher ⁸⁷Sr/⁸⁶Sr values than those in the springs issuing from granitic rocks containing biotite but no muscovite. Biotite is apparently more resistant to chemical reaction with the soda waters than is muscovite. The metamorphic rocks beneath the plutons are believed to be free of muscovite because of the low ⁸⁷Sr/⁸⁶Sr values. The waters of the soda springs have δD and δ¹⁸O identical with those of modern meteoric water but contain high chloride concentrations (up to 2500 mg/L). This combination requires mixing of meteoric waters with a brine of at least 100,000 mg/L chloride. Such brines are usually found in clastic rocks of marine origin. High boron

content (as much as 33 mg/L) and readily detectable Br⁻ and I⁻ confirm the presence of marine clastic rocks (now metamorphosed) beneath 11 of the springs.

INTRODUCTION

Considerable uncertainty exists in estimates of the thickness of granitic batholiths and in knowledge of the kinds of rocks that lie beneath them. The belief that batholiths have constant or increasing cross-sectional areas with increasing depth was first published by Dr. Suess (1895, p. 52). Press (1966, p. 196) wrote that unique interpretations of seismic studies in crustal terranes, in terms of materials, are rarely possible due to the overlap of velocity ranges for common geologic materials. The same uncertainty is inherent in gravity studies because of the overlap of specific gravities in common rock types (table 1). A further complication is the anisotropic nature of schistose and gneissic rocks where the velocity of seismic waves depends on the direction of travel (Birch 1960; 1961). Not only must mass and location be specified for the inclusion of schistose rocks in seismic models, the orientation of the schistosity must also be chosen. Even if the seismic velocity is known or assumed, the relation between velocity and density is not unique (Bate-man and Eaton, 1967, p. 1411). Interpretation of the nature of unexposed geologic materials based solely

Table 1.—Density and seismic velocity ranges of rocks
[From Press (1966). V_s is S wave velocity; V_p is P wave velocity; n.d. means not determined]

Rock	Density g/cc		V _s km/s		V _p km/s	
	Minimum	Maximum	Minimum (1 bar)	Maximum (10,000 bars)	Minimum (10 bars)	Maximum (10,000 bars)
Granite	2.62	2.68	2.77	3.70	4.70	6.61
Serpentine	2.60	2.79	2.71	3.83	4.7	7.15
Schist, mica	2.80		n.d.	n.d.	5.7	6.64
Schist, talc	2.91		n.d.	n.d.	4.9	6.97
			Pressure unknown		Pressure unknown	
Schist, chlorite	n.d.		3.27		4.89	

on geophysical studies of gravity and seismic velocity cannot produce unique solutions. The nature of the Sierra Nevada batholith at depth has been interpreted as igneous rock, based on gravity and magnetism (Oliver, 1977) and seismic velocity studies (Bateman and Eaton, 1967), but the nature of the basement rocks remains a matter of conjecture because these geophysical methods do not permit the distinction between various igneous and metamorphic rocks.

The geologic field relations are also ambiguous. Geologic maps of the plutons of the Sierra Nevada all show steeply dipping contacts (Ross, 1958; Peck, 1964; Bateman, 1965; Bateman and Moore, 1965; Huber and Rinehart, 1965; Kistler, 1966; Huber, 1968; Bateman and others, 1971; Lockwood and Bateman, 1976; Moore, 1978). The downward projection of the contacts is quite arbitrary. Either the outward extension of the plutons with depth to yield a batholith in the sense of Suess (1895) or inward to terminate the pluton at depth would fit the field observations. An example of the problem of extrapolating surface geologic observations to depth is shown by the detailed study of a small metamorphic mass in the central Sierra Nevada by Kistler and Bateman (1966). The authors specify that these rocks form a roof pendant, but on their cross section below a few hundred meters neither structural configuration nor rock type can be confidently interpreted. Hamilton and Myers (1967) wrote that heat production by radioactive decay in granitic rocks of the Sierra Nevada is high relative to heat flow (Lachenbruch, 1968; Lachenbruch and Sass, 1977, p. 653) suggesting less heat production in the rocks that underlie the plutonic rocks. These relations led Lachenbruch (1970) to suggest a change in the chemical composition of the rocks of the Sierra Nevada with depth.

One line of evidence for the nature of the unexposed rocks at depth in the Sierra Nevada is the chemical and isotopic compositions of fluids issuing from the natural springs in the range.

The isotopic composition of carbon dioxide (CO_2) has been used to identify metamorphism of marine carbonates as the source of CO_2 in mineral waters of Europe, Asia Minor, and the United States (Barnes and others, 1978). The marine carbonate source was identified because the isotopic compositions of the carbon-13 (^{13}C) are generally close to 0 permil, referred to the Pee Dee belemnite (PDB) standard. Marine carbonate is the source of some of the CO_2 at Karlovy Vary (Carlsbad) where the bedrock is granite because the ^{13}C values are enriched as much as +1.1 permil (PDB) (Barnes and O'Neil, 1974). Carbon dioxide from organic sources

is usually depleted more than -20 permil (Craig, 1953). Inclusions of CO_2 have been reported to be found in deep-sea basalts where the CO_2 can only be from mantle sources (Pineau and others, 1976; Moore and others, 1977). The range of ^{13}C compositions from the CO_2 -filled inclusions in deep-sea basalts range from -4.7 to -8.1 permil. For CO_2 issuing from the igneous and metamorphic terrane of the Sierra Nevada, a ^{13}C isotopic composition in the range -4.7 to -8.1 permil is more likely to be from a mantle source, and a value near zero permil is more likely to be from marine carbonate rocks.

Stetler and Allegre (1978) used $^{87}\text{Sr}/^{86}\text{Sr}$ values in water, among other chemical data, to determine the nature of the basement rocks beneath the volcanic rocks of the Cantal area, France. Barbieri and Tolomeo (1979) also used $^{87}\text{Sr}/^{86}\text{Sr}$ data to discriminate between volcanic and marine source rocks in a study of the strontium in travertines of Central Italy. $^{87}\text{Sr}/^{86}\text{Sr}$ values for seawater and marine carbonates have been reported by Peterman and others (1970) and Veizer and Compston (1974). Because the isotope ratios of strontium in seawater and marine carbonates vary with time of deposition, the ratio may serve as a test for the mineral source of strontium dissolved in the mineral water and for the ages of the source rocks.

Deuterium (D) and ^{18}O contents of water have long been used to identify meteoric water using the relation first established by Craig (1961). Enrichments of metamorphic water in D and ^{18}O have been reported by White, Barnes, and O'Neil (1973) and are of use in identifying nonmeteoric water. The chemical composition of waters from marine sediments have been characterized by White (1957) and have been used by White, Hem, and Waring (1963) to classify subsurface waters genetically. They pointed out that brines in evaporite-free, clastic rocks of marine origin are characterized by high bromide-chloride and iodide-chloride ratios and contain at least moderate amounts of boron. Such saline waters have been reported issuing from the metamorphic rocks of the Sierra Nevada (Mack and Ferrell, 1979). Presumably the saline water was present during metamorphism and is now being flushed by meteoric water.

Reaction states, whether equilibrium or regular departures from equilibrium, may also be used to identify origins of solutes in water. Low temperature CO_2 -rich waters react with serpentine to form magnesite, opal, and magnesium-rich waters just at saturation with amorphous silica at the temperature of the spring (Barnes and others, 1973). The saturation of spring water rich in magnesium with amorphous silica at low temperature is uniquely re-

Table 2.—Maximum concentrations of dissolved constituents in low temperature carbon dioxide springs of the Sierra Nevada

[Feth and others, 1964]

Constituent	Maximum concentration (mg/L)
SiO ₂	57
Ca	26
Mg	6.3
Na	15
K	4.5
HCO ₃	120
Cl	10

stricted to reactions among CO₂ gas, water, and serpentine. No other magnesium-rich, cold, CO₂-charged water from any other type of rock throughout the world (Barnes and others, 1978) yields saturation with amorphous silica.

The dissolved constituents in common meteoric water of the springs of the Sierra Nevada have been described by Feth, Roberson, and Polzer (1964) and in water from granites in the Sangre de Cristo Range, New Mexico by Miller (1961). The maximum concentrations of constituents are given in table 2. In the present study we have determined the dissolved constituents and isotopic compositions of waters from 22 soda springs (fig. 1) in the Sierra Nevada and Klamath Mountains; the locations of the CO₂-rich springs and the bedrock type at each spring are shown in table 3. The results of the analyses are used to infer some compositions of rocks at depth in the Sierra Nevada.

Because mercury deposits in the Coast Ranges of California are usually associated with CO₂-rich fluids (Barnes, Hinkle and others, 1973) analyses for mercury were made. Uranium analyses were made because uranium forms strong complexes with carbonate ions (Langmuir, 1978) and uranium deposits occur in the Sierra Nevada (MacKevett, 1960; Rapp, 1978). It is possible the CO₂-rich waters of the Sierra Nevada may be related to the ore-forming fluids.

METHODS

The chemical analytical methods used are those specified in Presser and Barnes (1974). In addition, the dissolved CO₂ species were precipitated by the injection of 20 mL of ammoniacal strontium chloride solution into 100 mL samples of water from a syringe through a 0.45 μm filter. The precipitates were transferred and washed with CO₂-free

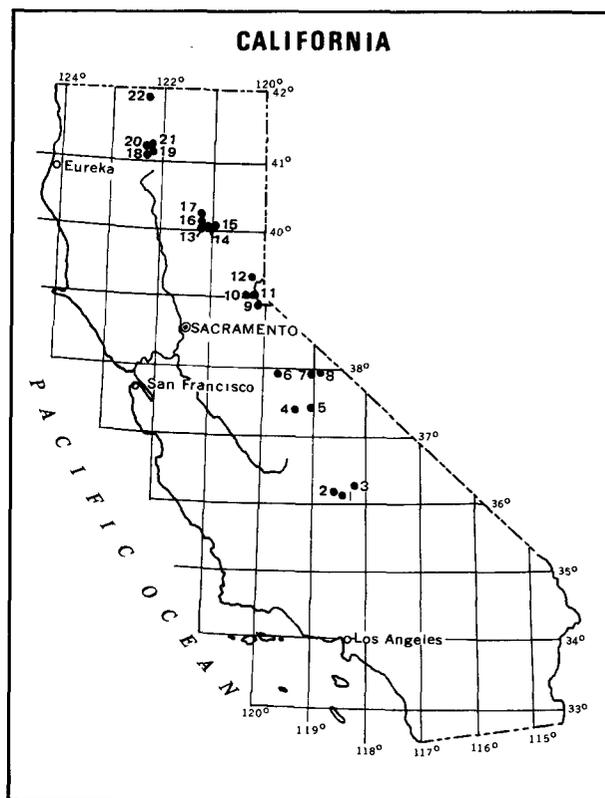


Figure 1.—Location of soda springs in the Sierra Nevada and Klamath Mountains.

water in an argon atmosphere glove box. The precipitates were dried and ground in a ball mill to homogenize them. The carbon, hydrogen, and oxygen isotope analyses were done by L. D. White in the laboratory of Dr. J. R. O'Neil. The ⁸⁷Sr/⁸⁶Sr values were determined by A. C. Robinson.

Water for uranium analyses was filtered through 0.1 μm pore-size filters. Two liters of filtrate were collected for each sample. The samples were then immediately acidified to a pH value of 2. The subsequent analyses, by the sodium fusion fluorescence method, (Thatcher and others, 1977) have a detection limit of 0.01 μg/L. In the field, samples to be analyzed for mercury were treated with a 2:1 mixture of concentrated sulfuric and nitric acids, potassium permanganate, and potassium persulfate to prepare for subsequent laboratory analysis by flameless atomic absorption (U.S. Environmental Protection Agency, 1971).

RESULTS

The analytical results are given in table 4 for the sample locations given in figure 1 and table 3. As a reference for the temperatures given, the mean annual air temperature at the Yosemite National

Table 3.—Location and bedrock geology of selected soda springs of the Sierra Nevada and Klamath Mountains
[Locations shown in figure 1]

Map number	Name	Location	Bedrock type	Reference
1	Camp Nelson	SW $\frac{1}{4}$ sec. 34, T 20S, R. 31E	Pre-Cretaceous limestone, granitic rocks undivided	Mathews and Burnett (1965).
2	Soda Spring	NW $\frac{1}{4}$ sec. 31, T. 20S, R. 31E	---- do -----	---- do -----
3	Jordan Hot Spring	SW $\frac{1}{4}$ sec. 33, T. 19S, R. 34E	Granitic rocks undivided	---- do -----
4	Soda Spring	NW $\frac{1}{4}$ sec. 30, T. 6S, R. 24E	Mount Givens Granodiorite	Huber (1968).
5	Devil's Post Pile	SE $\frac{1}{4}$ sec. 34, T. 3S, R. 26E	Cathedral Peak Granodiorite and andesite	Huber and Rinehart (1965).
6	Tuolumne Meadows	SW $\frac{1}{4}$ sec. 5, T 1S, R. 24E	Granitic rocks undivided	Strand (1967).
7	Mono Lake			
	Warm Spring	E $\frac{1}{2}$ sec. 18, T. 1N, R. 27E	Quaternary alluvium and pumice	Kistler (1966).
8	Mono Lake			
	Cold Spring	E $\frac{1}{2}$ sec 16, T. 1N, R. 27E	---- do -----	---- do -----
9	Glen Alpine	E $\frac{1}{2}$ sec. 9, T. 12N, R. 17E	Jurassic-Triassic volcanic rocks	Strand and Koenig (1965).
10	Wentworth	SW $\frac{1}{4}$ sec. 31, T. 13N, R. 15E	Granitic rocks undivided	---- do -----
11	Rubicon Soda Spring	E $\frac{1}{2}$ sec. 31, T. 14N, R. 16E	---- do -----	Burnett and Jennings (1965).
12	Summit Soda Spring	SW $\frac{1}{4}$ sec. 9, T. 16N, R. 15E	Granitic rocks undivided, Lower Jurassic marine metasedimentary rocks	---- do -----
13	Belden	SE $\frac{1}{4}$ sec. 23, T. 25N, R. 6E	Paleozoic marine metasedimentary rocks	Lydon and others (1960).
14	Twain	NE $\frac{1}{4}$ sec. 24, T. 25N, R. 9E	Paleozoic marine metasedimentary rocks, Paleozoic volcanic rocks	---- do -----
15	V and M Quarry	SW $\frac{1}{4}$ sec. 3, T. 25N, R. 9E	Paleozoic marine metasedimentary rocks	---- do -----
16	Soda Spring	NW $\frac{1}{4}$ sec. 17, T. 26N, R. 7E	Paleozoic marine metasedimentary rocks, Triassic marine metasedimentary rocks	---- do -----
17	Humbug Valley	NW $\frac{1}{4}$ sec. 6, T. 26N, R. 7E	Triassic marine metasedimentary rocks	---- do -----
18	Castle Rock	SW $\frac{1}{4}$ sec. 14, T. 38N, R. 4W	Devonian or pre-Devonian metavolcanic rocks	Strand (1963).
19	Castle Crag	NW $\frac{1}{4}$ sec. 12, T. 38N, R. 4W	---- do -----	---- do -----
20	Soda Spring	SW $\frac{1}{4}$ sec. 13, T. 39N, R. 4W	Mesozoic basic intrusive rocks	---- do -----
21	Shasta Soda Spring	NE $\frac{1}{4}$ sec. 13, T. 39N, R. 4W	---- do -----	---- do -----
22	Bogus Creek	SE $\frac{1}{4}$ sec. 13, T. 47N, R. 5W	Tertiary volcanic rocks	---- do -----

Park headquarters is 13°C (U.S. National Oceanographic and Atmospheric Administration, 1977).

The compositions of gases collected from the soda springs of the Sierra Nevada are given in table 5. The accuracy and completeness of the analyses improve with the more recently collected waters because of improvements in methods for both collection and analysis. The carbon-containing gas is chiefly CO₂, and there are small but variable amounts of methane. A sample of marble from the Dinkey Creek roof pendant (N $\frac{1}{2}$ sec. 14, T. 9 S., R 26E.) was analyzed for its ¹³C, ¹⁸O, and ⁸⁷Sr/⁸⁶Sr content. The $\delta^{13}\text{C}$ is 1.31 permil, PDB, the $\delta^{18}\text{O}$ is 22.06 permil, SMOW, and the ⁸⁷Sr/⁸⁶Sr is 0.70868.

DISCUSSION

Some of the soda springs of the Sierra Nevada are exceptionally rich in dissolved silica. Indeed, nearly half of them are near saturation with respect

to amorphous silica. The source of the high concentrations of silica is clearly not the plutonic rocks because some of the soda springs from granitic rocks are not saturated with amorphous silica and all the nonsoda springs are much lower in silica (fig. 2). Also shown in figure 2 is the temperature dependence of the solubility of amorphous silica (Kitahara, 1960). CO₂-rich waters react with lizardite-chrysotile serpentine in the Coast Ranges of California to form silica-carbonate rock (Barnes and others, 1973). These CO₂-rich waters are also shown in figure 2. They lie on the same trend and overlap in silica concentrations with the silica-rich spring waters of the Sierra Nevada. Silica concentrations in natural waters that correspond to the equilibrium with amorphous silica at low temperature and high magnesium concentrations are uniquely restricted to CO₂-charged waters reacting with serpentine. Examination of compositions of CO₂-charged waters during the compilation of CO₂ discharges of the world (Barnes and others, 1978)

revealed many waters from igneous terrains that are unsaturated with amorphous silica. Springs 9, 10, 14-17 and 22 are examples from this study.

The presence of serpentine in the Coast Ranges of California and the Sierra Nevada is demonstrated by the amorphous silica saturation and high magnesium concentrations in some of the CO₂ springs. However, the Mg²⁺ concentrations in the CO₂-rich springs of the Coast Ranges are all higher than those in the Sierra Nevada (fig. 3) at the same temperature, despite the same range of SiO_{2(aq)} and pH. The serpentine mineral in the Sierra Nevada is less soluble than the lizardite-chrysotile of the Coast Ranges; thus, it apparently is antigorite.

Many of the sample points in figure 2 lie on a solubility curve and show that the serpentine-CO₂-water reaction occurred at or near the temperature of the spring water at its orifice. The depth to the antigorite depends upon the thermal gradient between the subsurface antigorite and the spring orifice. If it is assumed that the ground water system is isothermal, then the depth to antigorite may be great. If, however, the ground water has the same thermal gradient as the rocks, a temperature gradient of 10°C per kilometer is indicated (Lachenbruch, 1968). With this gradient, all the suspected occurrences of antigorite serpentinite (except the ones below spring numbers 3 and 7) would be less than 1 km below the present surface. Obviously such an assumption is unlikely because many of the springs are at temperatures higher than the mean annual air temperature. These higher temperatures indicate convective heat flow, but the calculated temperature gradient (Lachenbruch, 1968) is for conductive heat flow only. The implication certainly remains, however, that the serpentine is not very far below the present surface.

The CO₂-rich waters of the Sierra Nevada are quite rich in calcium; they far exceed the 26 mg/L reported as a maximum for the nonsoda springs of the range (Feth and others, 1964). It is possible that calcite-bearing rocks are in contact with all the soda spring waters. Isotopic compositions of strontium in water from eleven of the springs are shown in table 4. The isotopic compositions of strontium in the waters issuing from granitic rocks are relatively nonradiogenic. As shown in table 6, some of the ⁸⁷Sr/⁸⁶Sr ratios, however, are consistent with strontium isotope ratios in seawater and marine carbonate rocks of late Paleozoic and early Mesozoic age. The strontium isotopic data from these are consistent with the water in the soda springs being in contact with and dissolving calcite derived from marine carbonate rocks included in or lying beneath the exposed granitic rocks, but strontium from locations

6, 10, 16 and 17 have isotopic compositions lower than any known Mesozoic or Paleozoic marine carbonate. In only two samples are the isotopic compositions of the strontium in the soda spring waters consistent with being derived from plagioclase in the granitic rocks traversed by the spring waters. The average initial strontium isotopic compositions of the granitoids in the region of the individual springs are shown in table 4. Plagioclase from specimens of the pluton which hosts the springs at locations 4 and 6 have a measured ⁸⁷Sr/⁸⁶Sr, the same as the strontium from the spring water (Kistler, unpublished data).

The ⁸⁷Sr/⁸⁶Sr ratios, 0.7101, 0.7274, and 0.7141, of three samples (map numbers 12, 14, 15) are very radiogenic. The soda waters yielding such high ratios are from the muscovite schists of the Feather River area. The radiogenic strontium is now being leached from the muscovite mica of the schists. The granitic rocks of the Sierra Nevada contain biotite mica, and these data give an important constraint to the rocks in contact with soda springs issuing from the plutonic rocks; they can contain no muscovite. The granitic rocks contain abundant biotite, but the biotite is apparently resistant to the chemical attack of the soda water whereas the muscovite is not. This observation is similar to that in a study of iron-rich ground water where Barnes and Back (1964) reported very low iron concentrations in water of low oxygen content from glauconite-bearing sands. The low iron concentrations indicate the stability or insolubility or unreactiveness of iron phyllosilicates in low oxygen waters, and are consistent with the failure of the biotites to yield strontium to the low oxygen (table 5) soda springs of the granitic rocks of the Sierra Nevada. The CO₂ effectively strips oxygen from the meteoric ground water.

More information concerning the rocks at depth in the Sierra Nevada can be gleaned from the chemical data. The water compositions given in table 4 show that the soda springs from the Sierra Nevada contain far more Cl⁻ than the nonsoda springs (Feth and others, 1964) which have a maximum Cl⁻ concentration of 10 mg/L. Despite the high Cl⁻, the waters are not much different in isotopic composition from meteoric waters (fig. 4) and show far less shift in ¹⁸O than is found in geothermal systems (Craig, 1963). Either the meteoric waters are leaching the evaporites or they are diluting the brines. Marine clastic rocks characteristically contain brines (White and others, 1963), and brines derived from evaporites lack I⁻, Br⁻, boron, and ammonia (White, 1957). As is shown in table 3, the waters with higher (>200 mg/L) chloride concentrations contain readily detectable I⁻, Br⁻, bo-

Table 4.—Composition of selected soda-spring waters of the Sierra Nevada and the Klamath Mountains

[Concentrations are given in mg/L except for U and Hg which are in $\mu\text{g/L}$, T. S. Presser and W. C. Evans, analysts. ^{13}C data are relative to PDB; ^{18}O and D data are relative to SMOW, L. D. White, analyst. $^{87}\text{Sr}/^{86}\text{Sr}$ analyses by A. C. Robinson. ($^{87}\text{Sr}/^{86}\text{Sr}$)_o is average initial strontium isotopic composition of plutons in the vicinity of the soda springs (Kistler and Peterman, 1973, 1978), unpublished data. U data from U.S. Geological Survey central laboratory, Denver, Colorado. $\delta^{18}\text{O}-\delta^{18}\text{O}_{\text{MW}}$ from equation $\delta\text{D}=8\delta^{18}\text{O}+10$. HCO_3 value is total alkalinity as bicarbonate. n.d. means not determined]

Map number	Sample number	Temp. °C	pH	δD	$\delta^{18}\text{O}$	$\delta^{18}\text{O}-\delta^{18}\text{O}_{\text{MW}}$	$\delta^{13}\text{C}$		$\text{SiO}_2(\text{aq})$	Na	K	U	Hg
							SrCO_3	$\text{CO}_2(\text{g})$					
1	CQ162RM77	17	6.12	-84.7	-12.2	-0.4	-3.79	-4.39	100	180	21	1.6	n.d.
2	CQ161RM77	17	6.13	-79.0	-11.4	-0.3	-4.51	-4.08	98	140	13	0.6	<0.1
3	CQ160RM77	43	6.15	-100	-12.4	+1.4	-2.09	-4.66	190	970	92	n.d.	n.d.
4	CQ163RM77	16	6.07	-92.5	-13.0	-0.2	-3.38	n.d.	100	910	46	129	<0.1
5	CQ159RM77	8	6.07	-107	-14.8	-0.2	-4.25	-5.80	76	400	20	48.9	n.d.
6	CQ68RM77	7.5	6.05	-121	-16.3	+0.1	-10.47	-9.01	67	220	5.7	n.d.	<0.1
7	GT113RM74	33	6.38	-126	-16.9	+0.1	-4.40	-6.56	130	410	34	56.8	<0.1
8	GT113RM74M	14	6.67	-128	-17.3	-0.05	n.d.	n.d.	90	64	9.0	n.d.	n.d.
9	GT80RM75	8	6.03	-99.6	-14.1	-0.4	-6.40	-8.52	45	350	9.5	54.7	<0.1
10	GT81RM75	15.5	6.02	-90.0	-12.8	-0.3	-7.49	-7.63	75	1250	32	1.1	<0.1
11	GT83RM75	10	6.01	-94.3	-13.5	-0.5	-8.33	-8.54	78	610	20	12.7	n.d.
12	GT79RM75	9.5	6.10	-95.0	-13.6	-0.5	-8.80	-9.33	87	280	27	0.5	n.d.
13	CQ62RM77	11	6.47	-78.6	-11.0	+0.1	-5.35	-9.88	100	790	35	<0.01	<0.1
14	CQ63RM77	39	6.48	-97.9	-13.0	+0.5	-5.98	-9.52	30	820	52	<0.4	0.5
15	CQ65RM77	14	6.50	-90.5	-10.8	+1.8	-2.70	-7.61	24	1150	120	<0.4	<0.1
16	CQ66RM77	10	6.06	-87.0	-12.2	-0.1	-9.18	-9.50	49	220	4.1	<0.5	<0.1
17	CQ67RM77	9.5	6.15	-91.5	-12.8	-0.1	-8.19	-8.80	61	170	2.1	<0.01	<0.1
18	GT57RM75	13.5	6.25	-78.8	-10.6	+0.5	-9.81	n.d.	86	975	21	n.d.	<0.1
19	GT56RM75	12	6.24	-80.3	-10.6	+0.7	-9.84	-13.24	76	1100	31	n.d.	<0.1
20	GT54RM75	10	6.03	-81.9	-11.5	0.0	-12.97	n.d.	79	425	21	n.d.	<0.1
21	CQ144RM77	13	6.64	-81.2	-9.68	+1.7	-6.18	-11.92	91	1150	43	n.d.	n.d.
22	GT52RM75	24	6.47	-82.3	-7.07	+4.5	-10.06	n.d.	72	3750	90	n.d.	n.d.

ron, and ammonia. They are derived, therefore, not from the leaching of evaporites, but from the brines present throughout much of the history of the marine sediments. Estimates of brine concentrations may be made by considering that some of the waters show no ^{18}O shift yet contain as much as 2,550 mg/L Cl^{1-} (map number 10, table 4). Chloride concentrations of 100,000 mg/L or more would be needed in the brine to yield so much chloride without affecting the isotopic composition of the rock. A plot of chloride concentration against $\delta^{18}\text{O}$ (fig. 5) shows no regularity, so it is not possible to deduce the isotopic composition of the brine from the data at hand although at granitic melt temperatures there will be little oxygen isotopic fractionation between minerals and rocks (Friedman and O'Neil, 1977).

The $\delta^{13}\text{C}$ values (table 4) from the soda springs in the Sierra Nevada are much more depleted in ^{13}C than the values reported from soda springs in Europe (Barnes and O'Neil, 1974;

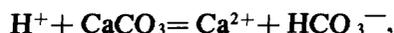
Buachidze and Buachidze, 1974; Cornides and Kecskes, 1974; Manfra and others, 1974, 1976; Dowgiallo and others, 1975; Panichi and Tongiorgi, 1975), and these values are centered on the -4.5 to -7.6 range of mantle-derived CO_2 (Pineau and others, 1976; Moore and others, 1977). Much of the CO_2 in the soda springs of the Sierra Nevada apparently comes from the mantle. The values of ^{13}C of the CO_2 gas and dissolved CO_2 species bracket the $\delta^{13}\text{CO}_2$ values of the total discharge. All the CO_2 -rich waters have reacted with plagioclase in the granitic rocks or have passed through calcite-containing rocks as shown by the high Ca^{2+} concentrations (table 4). Reaction with only plagioclase would not change the $\delta^{13}\text{C}$ of the CO_2 in the springs. A specimen of granitic rock near the springs at location 6 has been extensively altered; the alteration products are muscovite, chlorite, epidote and calcite. The granitic rock is a possible fossil conduit of a soda spring. The $\delta^{13}\text{C}$ of the calcite in this altered rock is -6.1 permil; that value indicates

Table 4.—Composition of selected soda-spring waters of the Sierra Nevada and the Klamath Mountains—Continued

[Concentrations are given in mg/L except for U and Hg which are in $\mu\text{g/L}$, T. S. Presser and W. C. Evans, analysts. ^{13}C data are relative to PDB; ^{18}O and D data are relative to SMOW, L. D. White, analyst. $^{87}\text{Sr}/^{86}\text{Sr}$ analyses by A. C. Robinson. $(^{87}\text{Sr}/^{86}\text{Sr})_0$ is average initial strontium isotopic composition of plutons in the vicinity of the soda springs (Kistler and Peterman, 1973, 1978), unpublished data. U data from U.S. Geological Survey central laboratory, Denver, Colorado. $\delta^{18}\text{O}-\delta^{18}\text{O}_{\text{MW}}$ from equation $\delta\text{D}=8\delta^{18}\text{O}+10$. HCO_3 value is total alkalinity as bicarbonate. n.d. means not determined.]

Map number	Sample number	Ca	Mg	Sr	HCO_3	H_2CO_3	Cl	SO_4	B	NH_3	Br	I	$^{87}\text{Sr}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_0$
1	CQ162RM77	390	59	n.d.	1,920	3,000	68	1	1.8	n.d.	n.d.	n.d.	n.d.	—
2	CQ161RM77	440	34	n.d.	1,810	2,700	79	3	2.0	n.d.	n.d.	n.d.	n.d.	—
3	CQ160RM77	110	38	n.d.	1,480	1,700	880	250	22	n.d.	1.6	1.6	n.d.	—
4	CQ163RM77	530	100	6.4	1,460	2,400	1,900	42	9.7	n.d.	3.7	3.4	0.7076	0.7075
5	CQ159RM77	130	32	n.d.	1,270	2,800	220	21	4.0	n.d.	n.d.	n.d.	n.d.	—
6	CQ68RM77	190	19	2.6	1,200	2,700	61	23	1.5	<1	n.d.	n.d.	.7065	.7064
7	GT113RM74	120	61	.68	1,560	1,200	105	28	6.1	<0.1	n.d.	n.d.	.7088	.7058
8	GT113RM74M	140	40	n.d.	816	410	18	4	1.3	0.7	n.d.	n.d.	n.d.	—
9	GT80RM75	275	54	1.2	1,140	2,500	550	10	4.7	<0.1	1.3	.4	0.7078	0.7050
10	GT81RM75	500	140	11	1,340	2,400	2,550	8	14	n.d.	2.9	2.3	.7065	.7050
11	GT83RM75	260	110	2.3	1,380	3,000	1,000	13	8.0	n.d.	1.8	1.1	.7068	.7050
12	GT79RM75	255	32	1.7	1,330	2,500	295	8	5.3	n.d.	.4	.2	.7101	.7050
13	CQ62RM77	620	170	5.0	3,950	2,800	520	120	40	1.0	.9	.4	n.d.	—
14	CQ63RM77	120	21	1.3	2,250	1,300	270	44	16	n.d.	1.0	.2	.7274	.7040
15	CQ65RM77	460	73	1.9	3,400	2,200	900	92	33	n.d.	1.7	1.6	0.7141	0.7040
16	CQ66RM77	270	54	2.6	1,620	3,300	46	5	4.6	0.1	n.d.	n.d.	.7061	.7040
17	CQ67RM77	390	23	1.7	1,690	2,800	58	4	6.1	<0.1	n.d.	n.d.	.7063	.7040
18	GT57RM75	170	190	n.d.	2,320	2,700	950	3	37	1.3	3.4	.8	n.d.	—
19	GT56RM75	180	230	n.d.	2,780	3,400	1,100	1	40	1.9	3.9	.6	n.d.	—
20	GT54RM75	120	94	n.d.	1,380	3,000	400	3	18	1.5	1.2	.2	n.d.	—
21	CQ144RM77	260	800	n.d.	6,740	2,900	800	67	60	n.d.	2.3	.5	n.d.	—
22	GT52RM75	160	57	n.d.	3,350	1,900	4,000	71	94	5.0	6.3	.8	n.d.	—

that the CO_2 involved in the alteration is from the mantle. If calcite alone supplied the Ca^{2+} in the waters, from the reaction



one bicarbonate ion accompanies each calcium ion dissolved from calcite. The highest Ca^{2+} concentration (map number 13, table 4) is 620 mg/L, therefore the corresponding HCO_3^- should be 930 mg/L. The same water contains 3,950 mg/L HCO_3^- and 2,800 mg/L H_2CO_3 so the contribution of the calcite to the dissolved carbon species is only about 14 percent. The $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ composition of a marble specimen from the Dinkey Creek roof pendant, 1.31 permil (PDB) and 0.70868 respectively, are in the normal range for marine limestones (Peterman and others, 1970; Craig, 1953). The carbon in the marble is far more enriched in $\delta^{13}\text{C}$ than the CO_2 in the soda springs. There would doubtless be enrichment to-

ward marine carbonate ^{13}C values to some extent in the ^{13}C owing to dissolution of marble and calcareous clastic metasedimentary rock. Carbonates in some contact metamorphosed rocks and in some marbles containing calcsilicates show a decrease in $\delta^{13}\text{C}$ relative to unmetamorphosed limestone with values as low as -3.0 permil (Shieh and Taylor, 1969). Calcite within an intrusion (Deines and Gold, 1969) has a $\delta^{13}\text{C}$ value of -5 permil. However, considering the lack of apparent change in the $\delta^{13}\text{C}$ of the Dinkey Creek sample, metamorphic decarbonation and solution of the marbles may be ruled out as sources for most of the CO_2 .

All the carbon isotope data indicate that the CO_2 in the soda springs is from a deep source, possibly the mantle. An obvious implication in deriving CO_2 from the mantle is that the CO_2 pressure must equal or exceed the total pressure from the mantle to the surface. The $\delta^{18}\text{O}$ composition, 22.06 permil (SMOW) of the marble from the Dinkey Creek locality, is in the range found for Precambrian, Cam-

Table 5.—Compositions of gases, in volume percent, from the carbon dioxide-rich springs of the Sierra Nevada and Klamath Mountains

Gas	Map number										
	1	2	3	4	5	6	7	8	9	10	11
He	<0.02	<0.01	<0.02	0.01	<0.02	<0.02	—	No sample	<0.01	<0.01	<0.01
H ₂	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	—	(no gas)	<0.01	<0.01	<0.01
Ar	0.02	0.02	<0.02	0.006	0.02	0.03	} 0.46		0.02	0.01	<0.01
O ₂	0.01	<0.01	0.05	0.03	0.03	0.02			0.33	0.10	0.01
N ₂	0.59	0.98	0.42	1.43	0.56	0.86	1.3		0.78	0.74	0.10
CH ₄	0.005	0.06	<0.005	0.003	0.005	<0.01	—		0.03	0.02	<0.002
CO ₂	99.41	99.26	99.05	98.73	98.17	99.06	96.6		98.76	98.90	100.06
C ₂ H ₆	<0.05	<0.01	<0.05	<0.01	<0.05	<0.05	—		<0.01	<0.01	<0.01
Total	100.04	100.32	99.52	100.21	98.78	99.97	98.4		99.92	99.77	100.17

Gas	Map number										
	12	13	14	15	16	17	18	19	20	21	22
He	<0.01	<0.02	<0.02	<0.02	<0.02	<0.02	—	—	No sample	<0.02	—
H ₂	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	—	—	(no gas)	<0.01	—
Ar	0.10	<0.02	<0.02	<0.02	0.02	0.06	} 0.35	} 0.53		<0.02	} 0.58
O ₂	<0.01	0.04	0.02	0.09	0.11	0.04					
N ₂	6.82	0.11	0.31	0.10	1.79	1.41	3.16	1.17		0.46	1.60
CH ₄	1.39	<0.01	0.02	<0.01	0.12	0.56	3.52	0.50		<0.005	<0.01
CO ₂	91.88	99.15	99.12	98.71	96.68	98.23	92.98	96.85		98.58	96.36
C ₂ H ₆	<0.01	<0.05	<0.05	<0.05	<0.05	<0.05				<0.05	
Total	100.19	99.30	99.47	98.90	98.72	100.30	100.01	99.05		99.24	98.54

brian, Silurian, Devonian, and Triassic limestones (Hoefs, 1973). The apparent preservation of the initial ⁸⁷Sr/⁸⁶Sr, ¹³C, and ¹⁸O of this marble indicates that the igneous events had no compositional effect on the marine carbonates exposed in roof pendants in the Sierra Nevada. The organic matter in the former marine sediments that contributed the ammonia and iodide to the brines may have contributed ¹³C-depleted CO₂ to the water. Possibly the tendency for ¹³C-depleted CO₂ to be discharged in the springs of the Klamath Mountains (table 4) is due to the persistence of organic material through greenschist (tremolite-chlorite-albite-quartz) metamorphism.

A point map (fig. 6) has been constructed for the Sierra Nevada and the Klamath Mountains showing the composition of the rocks postulated as being leached by the CO₂-rich water at depth. The concentrations used for inferring the rock types are: for antigorite serpentinite—high Mg²⁺ concentrations and near saturation with respect to amorphous silica; for muscovite-free marine clastic metasedimentary rocks—chloride more than 200 mg/L; and possibly for marble—calcium concentrations in excess of 100 mg/L. Those springs whose

measured ⁸⁷Sr/⁸⁶Sr values are lower than marine carbonate values are apparently only in contact with granitic rocks.

Although little uranium is expected from rocks such as amphibolite, serpentinite, and marble, uranium may be leached from more siliceous rocks. Rather high concentrations of uranium are found in some of the waters of the soda springs in the central Sierra Nevada, as shown on table 4. It is possible that CO₂-rich waters were the ore-forming fluids for the uranium deposits of the Sierra Nevada. It is unlikely the CO₂-rich waters yield mercury deposits; mercury is below the detection limit (0.1 μg/L) in all but one of the soda springs analyzed (table 4).

SUMMARY AND CONCLUSIONS

The waters of the soda springs in the Sierra Nevada have been analyzed chemically. From the silica and magnesium concentrations, it is concluded that many of the waters have reacted at shallow depths with unexposed serpentinite at the temperature of the water in the orifice of the spring. Because the Mg²⁺ concentrations are high, it is con-

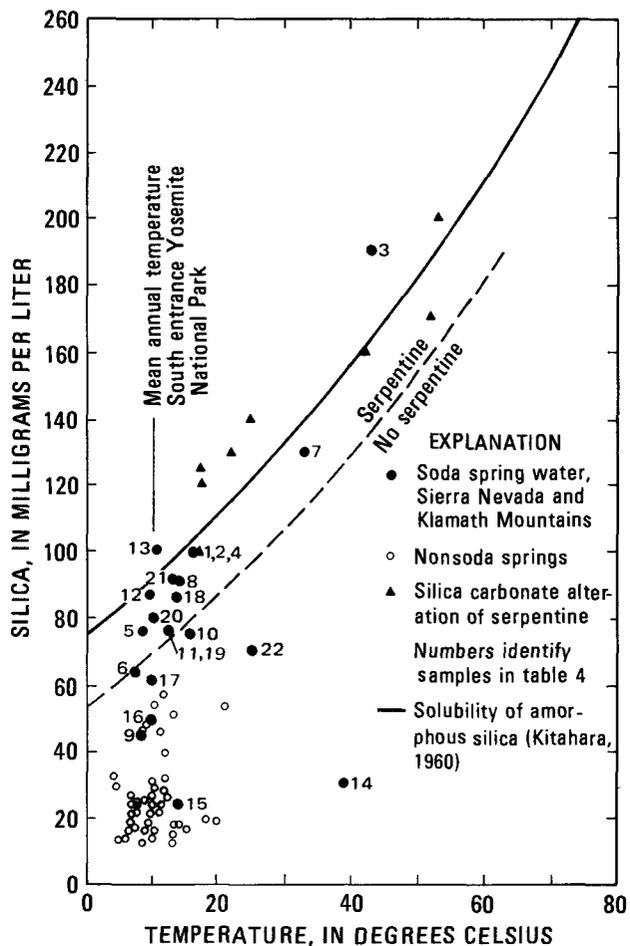


Figure 2.—Relationship between silica concentrations and temperatures in spring waters from the Sierra Nevada and Klamath Mountains.

cluded that the serpentine mineral is antigorite. Because the Ca^{2+} concentrations are all high, it is concluded that calcite or plagioclase has dissolved into the waters. $^{87}\text{Sr}/^{86}\text{Sr}$ analyses are compatible with the presence of marine carbonates of a Paleozoic and early Mesozoic age in the source areas of some of the springs. However, in other springs the Ca^{2+} and Sr^{2+} are probably derived from granitic rocks. Chloride, Br^- , I^- , boron, and NH_3 concentrations show that metamorphic rocks of a marine clastic origin also exist at depth. Isotopic composition of strontium in the springs from the granitic rock terrain indicates that muscovite is not a major phase in the marine clastic rocks in contact with the soda waters. The metamorphosed marine clastic rocks, therefore, may originally have had a mafic volcanic source. The Cl^- concentrations in the soda waters of meteoric water isotopic compositions require highly concentrated brines in the metamorphic rock. Possibly the brine in the marine clastic sedi-

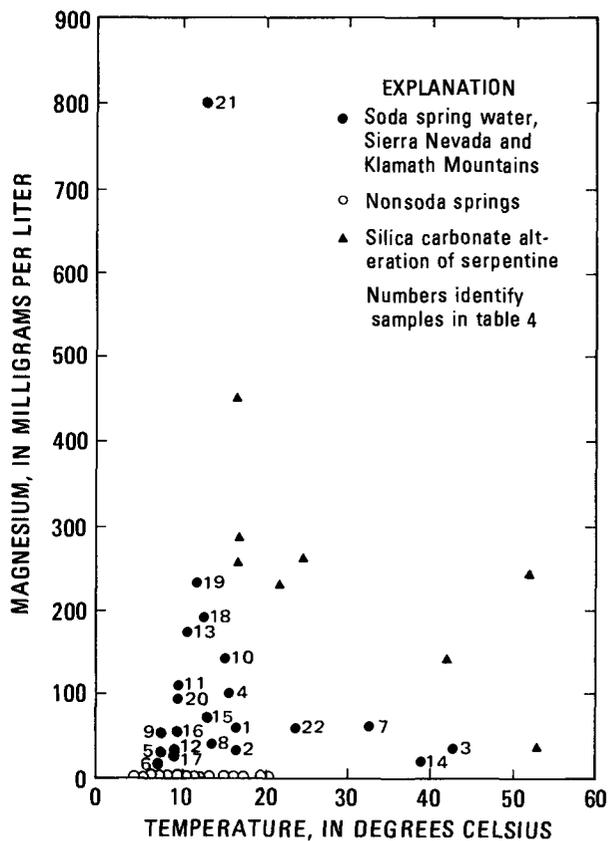


Figure 3.—Magnesium concentrations and temperatures of soda springs of the Sierra Nevada are indicated by (o). Magnesium concentrations and temperatures of soda-rich springs from the serpentines (lizardite-chrysotile) of the Coast Ranges of California are indicated by \blacktriangle .

Table 6.— $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of strontium in soda-spring waters and possible geologic ages of the limestones being dissolved

[From Peterman, Hedge, and Tourtelot, 1970]

Map number	$^{87}\text{Sr}/^{86}\text{Sr}$	Possible geologic ages
4	0.7076	Early or late Carboniferous, Triassic.
6, 10	.7065	Upper Jurassic.
7	.7088	Middle Carboniferous.
9	.7078	Devonian, early or late Carboniferous or Triassic.
11	.7068	Early or late Triassic.
14	.7274	None assigned; ^{87}Sr from micas.
15	.7141	None assigned; ^{87}Sr from micas.
17	.7063	Rather low; possibly Upper Jurassic.

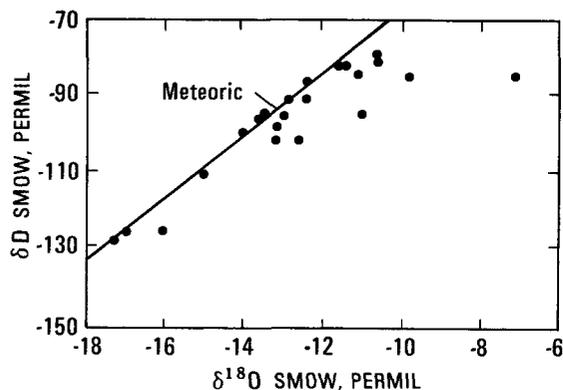


Figure 4.—Oxygen and deuterium isotopic compositions of soda springs of the Sierra Nevada and Klamath Mountains.

ments was the transporting medium to yield the gold and base metal deposits which are found in the metamorphic rocks of the Sierra Nevada rather than in the igneous rocks.

The rock suite that contributed to the chemistry of the soda springs (table 7) could have been an island arc whose metamorphic equivalent is now being leached by the CO₂-rich waters of the Sierra Nevada. It may be argued that all the springs are special cases and by extraordinary chance originated in small isolated masses of rocks in screens or septa of antigorite serpentinite, marble or other metamorphic rock within the plutons. The fact that 14 of the 17 CO₂-rich spring waters of the Sierra Nevada require rocks other than granitic rocks to explain their chemical properties means that there was an ubiquitous nongranitic component at some depth in the Sierra Nevada batholith. It is likely that the igneous rocks intrude and rest upon metamorphic rocks that contain marine sediments and that the granitic rocks have been injected into the marine sediments rather than being derived from them.

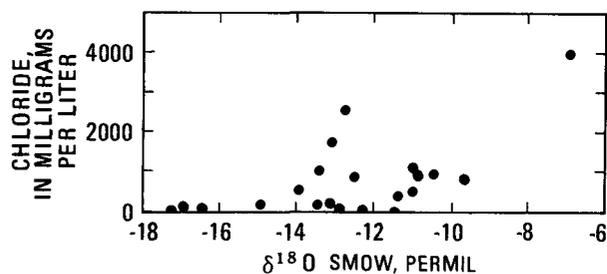


Figure 5.—Plot showing independence of chloride concentrations and oxygen-eighteen compositions of soda springs.

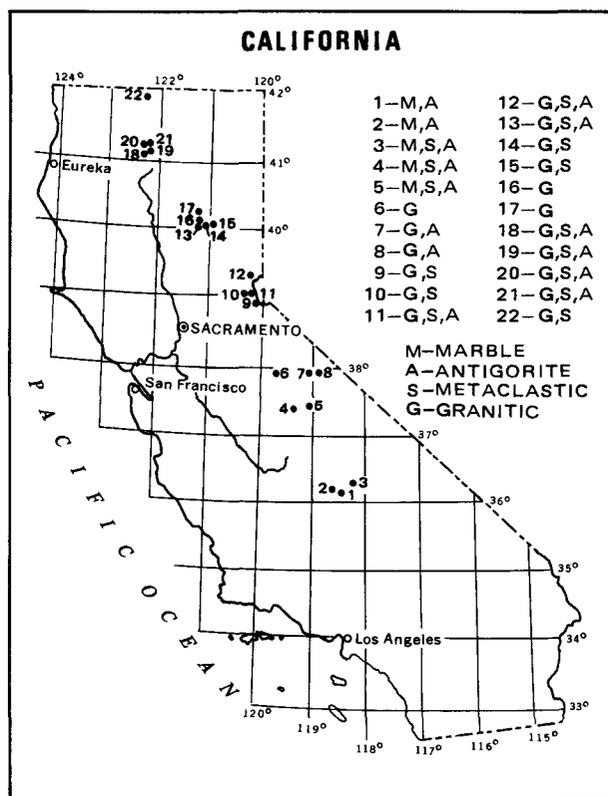


Figure 6.—Geologic map of the basement rocks of the Sierra Nevada, as inferred from geochemistry. Locations and exposed bedrock are given in table 3.

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Table 7.—Rock types beneath the soda springs of the Sierra Nevada and the Klamath Mountains

Map no. (fig. 1)	Marble	Granite	Metamorphosed marine sedimentary rocks		Antigorite
			Muscovite free	Muscovite bearing	
1	x	---	---	---	x
2	x	---	---	---	x
3	x	---	x	---	x
4	x	---	x	---	x
5	x	---	x	---	x
6	---	x	---	---	---
7	---	x	---	---	x
8	---	x	---	---	x
9	---	x	x	---	---
10	---	x	x	---	---
11	---	x	x	---	x
12	---	x	x	---	x
13	---	x	x	---	x
14	---	x	---	x	---
15	---	x	---	x	---
16	---	x	---	---	---
17	---	x	---	---	---
18	---	x	x	---	x
19	---	x	x	---	x
20	---	x	x	---	x
21	---	x	x	---	x
22	---	x	x	---	---

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