Chemical Composition of Naturally Occurring Fluids in Relation to Mercury Deposits in Part of North-Central California

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CONTRIBUTIONS TO ECONOMIC GEOLOGY

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A report of the chemical composition of waters, gases, hydrocarbons, sulfur, and rocks associated with mercury deposits

CONTENTS

ILLUSTRATION

TABLES

III

CONTRIBUTIONS TO ECONOMIC GEOLOGY

CHEMICAL COMPOSITION OF NATURALLY OCCURRING FLUIDS IN RELATION TO MERCURY DEPOSITS IN PART OF NORTH-CENTRAL CALIFORNIA

By Ivan Barnes, M. E. Hinkle, J. B. Rapp,
Chris Heropoulos, and W. W. Vaughn

ABSTRACT

The composition of fluids in the area studied displays a regional trend from chloride-rich waters east of the Stony Creek fault to bicarbonate-rich waters west of the fault although each fluid source must be regarded as a special case because of the local complexities of geology. Within the area studied are many mercury deposits. Although many examples were found of fluids presently causing silica-carbonate alteration, the usual wallrock alteration in mercury mines, none of the fluids sampled seem capable of forming commercial mercury deposits. The mercury concentrations in waters are all less than the acceptable limit for the mercury concentration of drinking water.
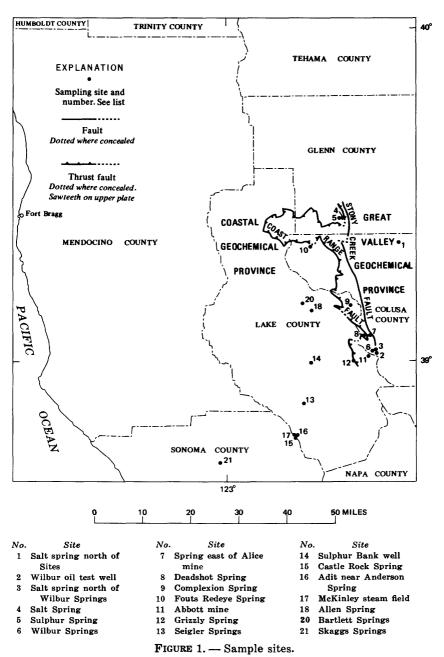
INTRODUCTION

The Coast Ranges of California have long been recognized as a favorable area for studying fluid-solid interactions in a wide variety of geologic processes. Early work, notably that of Waring (1915), described unusual fluids. Later work by White (1957) brought order out of seeming chaos. Studies of regional geology, especially those of Irwin (1960) and of Bailey, Irwin, and Jones (1964), provided a general geologic setting for subsequent work.

This report considers analyses of samples from 20 sites in Glenn, Colusa, Lake, and Sonoma Counties, north-central California. Materials sampled were ground water, steam condensates, tarry petroleum, and dissolved gases; analyses were made to determine major and minor constituents, including mercury. Although the complexity of the geochemical relations is obvious, some general comparisons and specific features of the fluid composition in relation to geology will be made. The trend from chloride-rich ground water east of the Stony Creek fault to chloride-bicarbonate rich water on the fault and to bicarbonate-rich water west of

the fault is also striking. The detailed geology of each locality, however, shows each fluid source to be a special case. Sampling locations in the homoclinal, structurally simple clastic marine sedimentary rocks of the Great Valley sequence of rocks of the Sacramento River valley serve as a reference. These fluids and rocks are not particularly unusual and serve as a basis for comparison with the more exotic fluids issuing from the structurally complex Stony Creek fault. The fluids from the Great Valley sequence also contrast with the very unusual fluids issuing from the structurally chaotic Franciscan terrane.

The location of sampling sites is shown in figure 1. Also shown in figure 1 is the surficial expression of the easternmost traces of the Coast Range fault (Bailey and others, 1970) and the Stony Creek fault (Brown, 1964, Rich, 1971). The Coast Range fault is usually expressed (Bailey and others, 1970) as, from west to east (structurally upward), Franciscan rocks in fault contact with the lower (ultramafic) part of an ophiolite sequence overlain by sedimentary rocks of the Great Valley sequence. The easternmost trace of the Stony Creek fault, between the ultramafic rocks and overlying Great Valley sequence, is a major geochemical boundary separating the Great Valley geochemical province to the east from the Coastal geochemical province to the west (fig. 1). The chemical composition of the waters from depth in the Great Valley geochemical province is characterized by high chloride to bicarbonate proportions. Along the trace of the Stony Creek fault, shown in figure 1, the waters are usually of a mixed chloride-bicarbonate type. West of the Stony Creek fault the waters are rich in bicarbonate. Locally the Franciscan rocks which lie west of the Coast Range fault are in structurally discontinuous blocks, poorly exposed and often mantled by landslide debris. Metamorphic grades may be irregularly distributed. In spite of the complex geologic relations west of the trace of the Coast Range fault shown in figure 1, virtually all the waters of the Coastal geochemical province are characterized by high bicarbonate to chloride proportions.

Extensive mercury production has taken place in the area studied (White, 1967), but most of the production has been from the Coastal geochemical province west of the eastern limit of the Stony Creek fault. Sulphur Bank (White and Roberson, 1962), the Western Mayacmas district (Bailey, 1946), the Eastern Mayacmas district (Yates and Hilpert, 1946), the Wilbur Springs district (Moiseyev, 1968), and the Skaggs Springs mercury mine (Everhart, 1950) are important examples.

Many of the mercury mines both in the area studied and else-

FIGURE 1. — Sample sites.

No.	Site	No.	Site	No.	Site
1	Salt spring north of Sites	7	Spring east of Alice mine	14	Sulphur Bank well
2	Wilbur oil test well	8	Deadshot Spring	15	Castle Rock Spring
3	Salt spring north of Wilbur Springs	9	Complexion Spring	16	Adit near Anderson Spring
4	Salt Spring	10	Fouts Redeye Spring	17	McKinley steam field
5	Sulphur Spring	11	Abbott mine	18	Allen Spring
6	Wilbur Springs	12	Grizzly Spring	20	Bartlett Springs
		13	Seigler Springs	21	Skaggs Springs

where are in silica-carbonate rock, which is an alteration product of serpentinite (Bailey and Everhart, 1964) in the Coastal geochemical province. Many of the mercury mines discharge bicarbonate-rich solutions that are shown (Barnes and others, 1973)

to alter serpentinite to silica-carbonate rock. The association of the fluids appropriate to yield silica-carbonate rock with economic mercury deposits led to the reasonable hypothesis that the bicarbonate-rich fluids may be related to the ore-forming fluid. As a consequence the fluids in the area were analyzed for their mercury concentrations in addition to an extensive suite of other major and minor elements.

ACKNOWLEDGMENTS

We thank Mr. Frederic D. Hanson for permission to sample in the Abbott mine, Turkey Run Tunnel, and we thank the Signal Oil Co. for permission to sample the McKinley steam-field condensates and well cuttings. Donald E. White collaborated in the fieldwork.

METHODS

Gases were collected in plastic syringes by displacement of the native water, and the syringes were carried to the laboratory immersed in a bottle of the native water. Gas analysis was by gas chromatography with helium as the carrier gas. A 6-foot by ¼-inch aluminum column of Porapak Q[1] (150–200 mesh) was used at temperatures between 22° and 26°C and flow rates between 50 and 56 cc per min (cubic centimeters per minute) to determine hydrogen, methane, ethane, and carbon dioxide. A 3-foot by ¼-inch aluminum column of Linde molecular sieve 13X was used at temperatures between 23° and 29°C and flow rates between 27 and 36 cc per min to determine hydrogen, oxygen, nitrogen, carbon monoxide, and methane. Steam condensates were obtained by condensing the steam in aluminum tubing immersed in a tank containing ice and water. The aluminum tubing did not accumulate a detectible amount of mercury. The condensate emerged at temperatures of 0°C to 2°C. Water samples were collected in 4-liter plastic bottles. Some samples were filtered through 0.45μ (micrometer) pore size ethyl acetate filters in a stainless steel pressure reservoir and stainless steel filter holder using nitrogen in high-pressure cylinders as a pressure source. A part of the filtered water was acidified to pH 2 with concentrated hydrochloric acid for analyses of calcium, magnesium, ammonium, aluminum, and iron. Another part of the filtered water was left untreated for analyses of silica, sodium, potassium, sulfate, chloride, fluoride, bromide, iodide, boron, and specific conductance. Bicarbonate and pH were determined at the sampling site by the

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[1] The use of brand names in this report does not constitute endorsement by the U.S. Geological Survey. Equivalent products can be used for the processes.

methods of Barnes (1964). Analytical procedures generally were those described by Brown, Skougstad, and Fishman (1970). The hydrogen sulfide content of condensate from the McKinley steamfield wells was determined in the laboratory and may be of questionable validity. Aluminum was determined by atomic absorption spectrophotometry, with 1,000 mg/l (milligrams per liter) potassium added to samples and standards.

Samples for mercury analysis were acidified to pH 1 with concentrated hydrochloric acid and analyzed by the procedure of Hinkle and Learned (1969). Water samples were filtered by suction through 0.45μ cellulose acetate filters.

Chemical precipitates from springs were analyzed for mercury by the mercury detector technique of Vaughn and McCarthy (1964). Sulfur interference in the precipitate samples was overcome by heating the samples and collecting the evolved mercury on a cool gold gauze, allowing the hydrogen sulfide to pass through the gold collector. The gold gauze was then heated to allow the mercury to pass into the detector.

Petroleum and tarry residues were analyzed for mercury both by an oxygen bomb procedure (Hinkle, 1971) and by a dithizone colorimetric procedure following acid digestion of the sample (Ward and McHugh, 1964) ; analytical results from both procedures showed good agreement.

Identification of solid phases were by X-ray diffraction and optical methods. Calcium-magnesium carbonate compositions were determined by determining the unit cell dimensions by least-squares refinement (Barnes and O'Neil, 1971).

GEOLOGY

The geologic relations are fairly simple in concept in a broad sense, with the Coast Range fault separating Great Valley sequence rocks from Franciscan rocks. Local relations, however, may not fit the larger relations, and the structural complexity of the Franciscan rocks may result in chaotic local geologic relations. The geochemical relations may be fully as complex.

Detailed descriptions of geologic materials found at the springs or wells are given in table 1. Some of the more important relations at the sampling sites are given in the following text, in the same sequence as in table 1. The sample localities are listed insofar as possible in a structural sequence. The sequence is from the Great Valley geochemical province farthest northeast of the Stony Creek fault to the Coastal geochemical province farthest southwest of the northeastern trace of the Stony Creek fault.

TABLE 1.—*Geology of sample sites*

Site	Location (County)	Bedrock Lithology	Bedrock Mineral assemblage	Deposit, if any, from water	Age and formation or rock unit	Attitude of rocks (if known) Strike	Attitude of rocks (if known) Dip	Reference for regional geology
				Sites in Great Valley sequence east of the Stony Creek fault (Great Valley geochemical province)				
Salt spring north of Sites, Calif.	SW¼ sec. 32, T. 18 N., R. 4 W., (Colusa).	Interbedded shale and sandstone.	Shale and sandstone similar. Quartz, plagioclase, white mica, chlorite.		Cretaceous, unit 7-C of Brown and Rich (1961).	N. 25° W.	25° W.	Brown and Rich (1961).
Wilbur oil test well.	NW¼ sec. 27, T. 14 N., R. 5 W., (Colusa).	Siltstone and mudstone.		Tarry petroleum residue.	Upper Jurassic or Lower Cretaceous, unit 1-C of Rich (1971).			Rich (1971).
Salt spring north of Wilbur Springs.	SE¼ sec. 21, T. 14 N., R. 5 W.	Calcareous conglomerate.	Calcite of the composition $CaCO_3$, plagioclase, quartz, chlorite.	Calcite of the composition $CaCO_3$.	Upper Jurassic or Lower Cretaceous conglomerate, unit 1-C of Rich (1971).	N. 5° E.	82° N.	Do.
				Waters yielded by rocks within the Stony Creek fault				
Salt Spring, Salt Valley.	NW¼ sec. 9, T. 18 N., R. 6 W., (Glenn).	Serpentinite overlying cataclastic graywacke, in part altered to rodingite.	Lizardite-chrysotile; quartz, albite, chlorite; xonotlite, hydrogrossular and calcite.	Calcite of the composition $Ca_{0.9}Mg_{0.1}CO_3$.	Upper Jurassic or Cretaceous.			Brown (1964).
Sulfur Spring, Salt Valley.	NE¼ sec. 8, T. 18 N., R. 6 W., (Glenn).	do	do	do	do			Do.
Wilbur Springs	NW¼ sec. 28, T. 14 N., R. 5 W., (Colusa).	Metachert overlain by serpentine.	Quartz with minor chlorite and albite.	Native sulfur; halite where water evaporates.	Upper Jurassic or Lower Cretaceous, unit 1-C of Rich (1971).			Rich (1971).
Spring east of Alice mine.	SW¼ sec. 5, T. 14 N., R. 5 W., (Colusa).	Serpentinite	Lizardite-chrysotile.	Very poorly crystallized hydromagnesite, dolomite and $Fe(OH)_3$.	Unknown			Do.

Name	Location	Host rock	Mineralogy	Composition	Age	Strike	Dip	Reference
Deadshot Spring.	SW¼ sec. 6, T. 14 N., R. 5 W., (Colusa).	do	do	Calcite rich in $MgCO_3$ but of such poor crystallinity the $MgCO_3$ content cannot be determined by X-ray methods.	do	....	....	Do.
Complexion Spring.	SW¼ sec. 3, T. 15 N., R. 6 W., (Lake).	do	do	A gel whose dry weight composition is: Wt. % MgO..........93.36 SiO_2..........6.36 Al_2O_3..........01 FeO..........23 CaO..........01 Na_2O..........02 B_2O_3..........01	do	....	....	McNitt (1968).
Fouts Redeye Spring.	SW¼ sec. 5, T. 17 N., R. 7 W., (Colusa).	Serpentinite in fault contact with cataclastic graywacke.	Lizardite-chrysotile in serpentine; quartz, albite, chlorite, and white mica in graywacke.	$Fe(OH)_3$	Upper Jurassic or Cretaceous sedimentary rocks.	N. 50° W.	NE. 50°	Brown (1964).
Abbott mercury mine.	NW¼ sec. 32, T. 14 N., R. 5 W., (Lake).	Fault gouge in serpentinite, heavy oil and water.	Opaline silica and magnesite after serpentinite.		Unknown.	....	....	Rich (1971).
Grizzly Spring	SW¼ sec. 2, T. 13 N., R. 6 W., (Lake).	Cache Formation of Anderson (1936) thrust over serpentine.	Not exposed	Dolomite of the composition $Ca_{0.6}Mg_{0.4}CO_3$.	Pliocene or Pleistocene Cache Formation of Anderson (1936).	....	....	Anderson (1936).
Seigler Springs	NE¼ sec. 24, T. 12 N., R. 8 W., (Lake).	Opaline (β-cristobalite) alteration of serpentinite.	β-cristobalite	$Fe(OH)_3$	Unknown	....	....	Brice (1953), Swe and Dickenson (1970).
Sulphur Bank steam well.	NW¼ sec. 5, T. 13 N., R. 7 W., (Lake).	Franciscan graywacke overlain by lake deposits overlain by Quaternary augite andesite.	Franciscan graywacke: quartz, chlorite, white mica, halloysite, and alunite.		Mesozoic (Franciscan) and Holocene.	....	....	White and Roberson (1962), Everhart (1946), and Brice (1953).

TABLE 1.— *Geology of sample sites*—Continued

Site	Location (County)	Bedrock		Deposit, if any, from water	Age and formation or rock unit	Attitude of rocks (if known)		Reference for regional geology
		Lithology	Mineral assemblage			Strike	Dip	
			Sites in Franciscan rocks west of the Stony Creek fault (Coastal geochemical province)					
Adit near Anderson Spring.	SW¼ sec. 26, T. 11 N., R. 8 W., (Lake).	Chert..........	Quartz, albite, and white mica.	Fe(OH)$_3$........	Mesozoic...........	N. 65° W.	S. 42°	Swe and Dickenson (1970).
McKinley steam field.	SW¼ sec 26, T. 11 N., R. 8 W., (Lake).	Franciscan interlayered graywacke (low textural zone 2), metachert, and greenstone; minor serpentinite.	Graywacke: albite, quartz, chlorite, white mica, calcite, dolomite at shallow depth. Chert: quartz, chlorite, albite, riebeckite, aegirine. Greenstone: albite, chlorite, white mica, augite, calcite. Lizardite-chrysotile: serpentinite with minor calcite veins in part bearing cinnabar. Above rocks have irregularly distributed lawsonite, glaucophane, and tremolite. Alteration in steam producing zone is kaolin after albite.	Amorphous silica from steam.	........do.......	....	....	Do.
Castle Rock Spring.	SW¼ sec. 26, T. 11 N., R. 8 W., (Lake).	Franciscan porphyritic volcanic and graywacke; hydrothermal alteration at spring.	Altered porphyry: albite, chlorite, montmorillonite, jadeite, lawsonite. Altered graywacke: montmorillonite, quartz, albite, white mica.	....	........do...	....	....	Do.

Allen Spring	SW¼ sec. 8, T. 15 N., R. 7 W. (Lake).	Andesite: andesine, augite, laboradorite phenocrysts. Andesite in part altered to montmorillonite, halloysite, and opal.		$Fe(OH)_3$		McNitt (1968).
		Interbedded shale and sandstone of the Great Valley sequence in contact with serpentine and metavolcanic rocks.	Great Valley sequence: quartz, albite, chlorite, white mica. Metavolcanic rocks: albite, quartz, chlorite, pumpellyite, white mica, calcite. Serpentinite: Lizardite-chrysotile.	...do...		McNitt (1968).
Bartlett Springs	NW¼ sec. 2, T. 15 N., R. 8 W. (Lake).	Greenstone, fine-grained graywacke, and serpentine. Structural relations unknown.	Greenstone: albite, chlorite, clinopyroxene, calcite. Graywacke: quartz, albite, chlorite, muscovite. Serpentine: lizardite-chrysotile.	Mesozoic(?)	$Fe(OH)_3$	McNitt (1968).
			Site in Coastal belt rocks (Coastal geochemical province)			
Skaggs Springs	SE¼ sec. 24, T. 10 N., R. 11 W.	Great Valley sequence.	Quartz, albite, orthoclase, kaolin, and muscovite.	Mesozoic	$Fe(OH)_3$	N. 75° E. 56° SW. Everhart (1950).

The salt spring north of Sites, Calif., issues from the Salt Lake fault (Brown and Rich, 1961). Wilbur oil test well and the salt spring north of Wilbur Springs issue from the eastward dipping homoclinal sequence of Great Valley rocks east of the Coast Range fault (Rich, 1971).

Many of the waters issuing from the Stony Creek fault are described as issuing from serpentinite or its equivalents. The ultramafic rocks are structurally beneath the ophiolite sequence according to Bailey, Blake, and Jones (1970). Where the fluids issue from the fault, part of the fluids may be from the Great Valley sequence and part may be from the Franciscan rocks.

The occurrence of rodingite in the cataclastic graywacke found in Salt Valley has structural significance. As Barnes and O'Neil (1969) and Barnes and others (1973) showed, rodingites are formed during episodes of serpentinization. The ultramafic body was in part still fresh when placed in contact with the graywacke and underwent serpentinization later as the serpentinizing fluid flowed across the contact into the graywacke.

Complexion Spring issues from lizardite-chrysotile serpentinite and deposits brucite and a magnesia-silica gel (Luce, 1971); it appears to be affected by serpentinization by the criteria of Barnes and O'Neil (1969).

TABLE 2. — *Composition of ground*

[Minerals stated in milligrams

Sample	SiO_2	Al	Fe	Ca	Mg	Na	K	NH_4
Salt spring north of Sites.........	17	0.4	0.4	8,850	79	9,500	40	18
Wilbur oil test well......................	.5	.29	<0.02	580	92	6,700	55	17
Salt spring north of Wilbur Springs.....................................	130	.3	6.2	490	228	4,600	255	135
Salt Spring, Salt Valley.............	140	.51	.13	115	262	8,400	90	155
Sulfur Spring, Salt Valley.........	54	.26	.16	48	68	890	15	20
Wilbur Springs..........................	200	.2	.04	2.8	38	8,500	440	280
Spring east of Alice mine..........	95	<0.1	.04	8.8	300	860	84	34
Deadshot Spring...........................	120	.1	2.1	160	345	2,000	164	105
Complexion Spring......................	24	<0.1	.06	.7	.8	12,000	350	210
Fouts Redeye Spring....................	125	<0.1	2.5	104	254	3,800	56	30
Seigler hot spring........................	170	.66	.22	30	238	162	20	12
Seigler lukewarm spring (The Geyser)...........................	160	.33	.60	21	140	212	40	10
Abbott mercury mine[1]...............	116	1.6	.0	64	443	1,500	39	22
Grizzly Spring[2]...........................	56	......	.1	135	712	2,720	53	1.7
Anderson Spring adit..................	50	.3	3.7	78	34	28	6.6	11.5
McKinley steam well 1................	8	.1	.12	1.1	.1	1.9	.1	86
McKinley steam well 3................	.2	<0.02	.05	.3	.05	.1	<0.1	107
Castle Rock Spring......................	125	.08	<0.02	14	1.9	64	3.2	.5
Sulphur Bank well.......................	140	.1	.38	19	40	1,310	41	490
Allen Spring.................................	44	.32	<0.02	78	162	24	1.6	.1
Bartlett Springs..........................	100	.54	<0.02	67	286	10	.8	.14
Skaggs spring 1............................	133	......	......	13	4.6	955	31	2.0
Skaggs spring 2............................	127	......	......	14	4.7	930	31	2.2
Skaggs Springs well....................	77	......	......	19	5.8	1,060	42	2.6

[1] Locality no longer accessible. Analysis from White, Hem, and Waring (1963).
[2] Data from U.S. Geol. Survey files, C. E. Roberson, analyst.

Castle Rock Spring and the McKinley steam-field fluids issue from a melange of Franciscan rocks. Graywacke, greenstone, chert, and serpentine are all represented in cuttings from McKinley well 1. Less than a mile north of the steam field is Lincoln Rock, a block of isolated blueschist in a landslide. The serpentinite found at shallow depth contains cinnabar in calcite veins. Kaolin is the alteration product of the albite in the graywacke of the steam-producing zone.

Skaggs Springs issue from rocks of the Coastal belt of Irwin (1960). Coastal belt rocks share many of the features of both Franciscan and Great Valley sequence rocks and may be regarded as intermediate between the Franciscan and Great Valley sequence rocks. It is not surprising that the fluids should be similar to the fluids issuing from the contact between Franciscan rocks and Great Valley sequence rocks.

RESULTS OF CHEMICAL ANALYSES

The results of analyses for major elements are given in table 2. Regional variations in water compositions are discernible but are complicated by the regional geologic relations. Both the Salt Spring north of Sites and the Wilbur oil test well are northeast of the eastern limit of the surficial expression of the Stony Creek

water and steam condensates

per liter. NA, not available]

HCO_3	CO_3	SO_4	Cl	F	Br	I	B	H_2S	Specific Conductance (mmhos/cm at 25°C)	pH	Temp. (°C)
21	0.02	130	30,900	0.6	160	70	17	......	64,700	6.89	18
62	2	72	11,400	.4	41	34	23	......	28,200	8.60	21
2,040	2	31	8,300	.7	33	23	250	......	23,800	7.04	22
3,150	39	63	11,800	1.4	45	50	200	NA	32,300	8.11	19
866	.9	54	1,210	.1	....	....	17	12	4,770	7.18	22
7,130	6	390	9,700	2.5	16	27	310	190	33,000	6.87	55
1,840	41	5.8	1,240	<0.1	7	3.3	40	......	5,890	8.40	18
3,280	7	6	3,140	.5	9	8	110	......	12,300	7.31	18
7.1	889	60	18,200	.5	70	50	20	3	47,300	12.07	9.5
5,000	30	7.0	3,990	1.1	22	6	115	......	16,000	7.88	15
1,320	1.2	6.3	272	<0.1	2	.7	19	......	2,530	6.88	50
900	1.5	7.2	297	<0.1	2	.5	17	......	2,160	7.22	44
2,710	......	467	1,900	1.0	3.8	6.3	56	<1	8,960	7.1	26
4,490	......	4.8	3,940	......	13	12	178	......	14,700	7.2	18
233	.1	283	3.0	.3	......	<0.1	.11	......	860	6.74	41.5
206	.04	133	10	<0.1	<0.1	<0.1	.45	3	556	6.48	>100
303	.05	36.3	23	<0.1	<0.1	<0.1	<0.01	11	715	6.37	>100
192	2	24.4	6	.6	<0.1	<0.1	.72	......	356	8.14	53.5
2,090	16	1,630	782	.8	6	1	620	NA	7,880	7.95	85
1,010	.4	17.5	26	<0.1	<0.1	<0.1	.44	......	1,440	6.77	13
1,640	.5	2.2	4.4	<0.1	<0.1	<0.1	.08	......	2,080	6.61	17
2,450	......	6	56	10	......	......	85	......	3,430	6.87	55
2,440	......	3	57	10	......	......	91	......	3,430	6.92	54
2,880	......	5	60	10	......	......	97	......	3,960	6.72	24

fault and show the high chloride:bicarbonate ratio commonly found in waters issuing from Great Valley sequence rocks. The chloride-rich waters are connate as defined by White (1965).

The salt spring north of Wilbur Springs and the Salt Spring in Salt Valley, Wilbur Springs, the spring east of the Alice mine, Deadshot Spring, Fouts Redeye Spring, the Abbott mine, and Grizzly Spring are on or very close to the Stony Creek fault, and the water analyses show subequal concentrations of chloride and bicarbonate. The fluids are considered in part connate modified by metamorphic reactions (White, 1957; Barnes, 1970).

Complexion Spring has an unusually high pH. In spite of the marked difference in chemical composition between Complexion Spring and the calcium hydroxide type waters probably resulting from present-day serpentinization (Barnes and O'Neil, 1969), the reaction state with respect to olivine, pyroxenes, brucite, and serpentine is the same for Complexion Spring water as for the calcium hydroxide type water. In spite of the high pH due to reactions with enstatite and forsterite and of the Mesozoic age of the source rocks, the sodium, potassium, chloride, bromide, and fluoride of Complexion Spring are remarkably close to the concentrations found in present-day ocean water, although the youngest rocks exposed are Cretaceous (Rich, 1971). As is characteristic of the moderately saline waters of California, ammonia and iodide are high, presumably because of decay of marine organisms.

The Seigler Springs are both much richer in bicarbonate than in chloride. Whether the chloride content is contributed by the surrounding Great Valley sequence rocks (Swe and Dickinson, 1970) or whether both the bicarbonate and the chloride are from the presumably underlying Franciscan rocks is not known. The steam condensates from the McKinley steam wells and water from the Anderson and Castle Rock Springs are entirely from Franciscan rocks and have anomalously high bicarbonate for local meteoric water from Franciscan rocks. The steam is dry—that is, it does not entrain liquid water; nonvolatile cations are therefore quite low. The sulfate is in large part from the oxidation of hydrogen sulfide subsequent to sample collection. Later field analyses by L. Willey from a different steam well show more than 100 mg/l hydrogen sulfide in the freshly collected steam condensate. The chloride of the steam condensates is higher in concentration than that of the spring waters. Possibly this relation indicates loss of some of the undissociated hydrogen chloride ($HCl°$) from depth rather than the evaporation of chloride-containing water because of very low values of cations other than ammonia. The slower natural upflow yields lower chloride because of dissociation of

HCl° at lower temperatures. The volatile constituents—carbon dioxide, hydrogen sulfide, and ammonia—are also lower, probably owing to condensation in the upper part of the vapor-dominated system (White and others, 1971).

Allen Spring and especially Bartlett Springs show extreme examples of fluids from the Franciscan rocks. Bartlett Springs are inferred to discharge locally derived meteoric water on the basis of sodium, potassium, ammonia, sulfate, chloride, fluoride, bromide, iodide, and boron concentrations and ratios. To the locally derived meteoric water has been added carbon dioxide from the presumably underlying Franciscan rocks. The carbon-dioxide-rich water alters serpentine to silica carbonate rock, removing magnesium, calcium, iron, and silica (Barnes and others, 1973). The iron in solution in both Bartlett and Anderson Springs is below detection because the discharges are so slow that the iron is entirely precipitated, as shown by the copious sludge of ferric hydroxide in the spring orifices.

The Skaggs Springs and well issue fluids from coastal-belt rocks. The coastal-belt rocks are intermediate in character (Irwin, 1960) between Franciscan and Great Valley sequence rocks. Certainly, the chloride is higher than in Bartlett Springs but not as high as in waters on the Coast Range fault.

RESULTS OF GAS ANALYSES

The results of gas analyses are given in table 3. Not all the springs discharge gases. A rough indication of atmospheric contamination is the oxygen content of the gases as analyzed. Nitrogen contents are partly atmospheric, but nitrogen is also a component of gases issuing from depth as distinct from air (Rudkin, 1968, p. 123). Hydrocarbon gases are produced in large quantity from Great Valley sequence rocks. The gas issuing from the salt spring north of Sites is an example of the hydrocarbon gases from the Great Valley sequence rocks. Along the easternmost expression of the Stony Creek fault are found gases rich in carbon dioxide (salt spring north of Wilbur Springs) or rich in methane (Salt Spring in Salt Valley). More common are carbon-dioxide-rich gases such as issue from Wilbur, Deadshot, Fouts Redeye, Grizzly, and Seigler Springs and the Sulphur Bank well. The hydrogen in the discharges of the wells is released from the water during oxidation of well casing and may constitute a major fraction of the gases discharged. Different gas compositions are found in adjacent wells and from the same well at different times (table 3). In spite of the fact that the McKinley steam wells are entirely in Franciscan rocks, there is a large methane component,

TABLE 3. — *Results (in volume percent) of analyses of gases*

	O_2	N_2	CH_4	CO_2	Other
Salt spring north of Sites	0.9	5.8	94	0.2	
Salt spring north of Wilbur Springs	.4	.9	2.0	98	
Salt Spring, Salt Valley	1.9	9.2	57	32	
Wilbur Springs	....	....	7	93	
Deadshot Spring	.4	1.0	1.9	95	
Fouts Redeye Spring	2.1	2.5	.06	92	
Grizzly Spring	.3	.8	1.0	97	
Seigler hot spring	1.2	2.3	3.0	92	
Seigler lukewarm spring	1.6	4.6	15	79	
Sulphur Bank well	2.9	16	24	59	$H_2=1.6$
McKinley 1 steam well, 17 March 70	.5	2.5	5.7	38	$H_2=50$
McKinley 1 steam well, 24 March 70	.1	3.4	7.9	31	$H_2=60$
McKinley 3 steam well, 17 March 70	1.3	6.0	8.3	28	$H_2=60$
McKinley 3 steam well, 24 March 70	.7	6.6	14	10	$H_2=73$
Skaggs spring 1	1.2	4.4	28	69	$C_2H_6=0.26$
Skaggs spring 2	2.1	5.1	21	76	$C_2H_6=0.13$
Skaggs Springs well	1.7	13	52	38	

especially after correcting for dissolved air and hydrogen from well-casing reactions. Methane may also be the major component in the gases discharged from coastal-belt rocks.

The results of the gas analyses show regional trends. It is safe to say that the highest methane:carbon dioxide ratios are found in gases from the Great Valley section. It is also safe to say that the highest carbon dioxide:methane ratios are found from the Stony Creek fault westward but that methane may be the dominant component in some places. The proportions of carbon dioxide to methane cannot be explained in detail because the relative amounts in deeper reservoirs are unknown. The rates of gas flow are complicated by the relative solubilities (carbon dioxide is 10 times as soluble as methane in water) and also by the fact that carbon dioxide may hydrolyze and further react.

MINOR ELEMENT ANALYSES

As noted in the introduction, the fluids studied include the carbon-dioxide-rich fluids that may cause the silica-carbonate alteration of serpentinite. The silica-carbonate rock is commonly the host rock of mercury deposits in California. Samples were analyzed for mercury, and the results are given in table 4. In spite of their close association with mercury deposits and, even more surprising, the fact that they include some that cause the usual wall-rock alteration, the fluids studied are low in mercury. Even the analyzed condensate of the dry steam from wells is quite low, although cinnabar has been found in cuttings from the

TABLE 4. — *Mercury content of samples*

[nd, not detected]

Sample	Hg $(\mu g/l)$
Wilbur oil test well, unfiltered	0.2
Salt spring north of Wilbur Springs, unfiltered	.1
Salt Spring, Salt Valley, unfiltered	nd
Sulfur Spring, Salt Valley, unfiltered	nd
Wilbur Springs, unfiltered	1.5
Spring east of Alice mine, unfiltered	nd
Deadshot Spring, unfiltered	nd
Complexion Spring, unfiltered	1.5
filtered	.1
Fouts Redeye Spring, unfiltered	nd
Seigler hot spring, unfiltered	nd
Seigler lukewarm spring, unfiltered	nd
Abbott mine water, unfiltered	1.0
filtered	nd
Grizzly Spring, unfiltered	nd
Anderson Spring adit, unfiltered	nd
McKinley steam well 1, variable condensation temperature,	
unfiltered	.5
variable condensation temperature, filtered	.2
condensed to 0°C, unfiltered	3.0
condensed to 0°C, filtered	nd
McKinley steam well 3, variable condensation temperature,	
unfiltered	.9
variable condensation temperature, filtered	.7
condensed to 0°C, unfiltered	1.0
condensed to 0°C, filtered	.1
Castle Rock Spring, unfiltered	nd
filtered	nd
Sulphur Bank well, unfiltered	1.5
filtered	.5
Allen Spring, unfiltered	nd
Bartlett Springs, unfiltered	nd
Skaggs spring 1, filtered	.09
algal material (dry weight)	1×10^4
sediment (dry weight)	4×10^4
Skaggs spring 3, filtered	.07
Skaggs Springs well, filtered	<.05
algal material (dry weight)	2
sediment (dry weight)	.08
Little Warm Springs Creek above Skaggs Springs, filtered	<.05
filtered	.05

one well examined petrographically. All materials analyzed contained less than 5 $\mu g/l$ (micrograms per liter), the maximum considered safe for drinking water by the U.S. Public Health Service.

Evidently, most mercury in the economic deposits of the area studied was not transported by fluids like those analyzed. The silica in water yielded by graywacke and greenstone is 20 to 50 mg/l but is much higher in carbon-dioxide-rich water from silica-carbonate rock or serpentinite. Silica and magnesium are being leached from serpentinites to form silica-carbonate rock (Barnes and others, 1973). Even if 10 mg/l silicate is leached from the silica-carbonate rock, the 1 $\mu g/l$ of mercury available for precipitation has at most 0.01 percent the volume of rock being leached. The

continued discharge of the fluids studied will leach rocks rather than form economic deposits.

In spite of the low mercury concentrations, most of the waters that contain both mercury and hydrogen sulfide are supersaturated with respect to both black (metacinnabar) and red (cinnabar). The solubility data of Barnes, Romberger, and Stemprok (1967) and the composition of Wilbur Springs with its remarkably high concentration of 190 mg/l of total sulfide sulfur and near neutrality (table 2) indicate that equilibrium concentrations of mercury species may be calculated. In table 5 are given solubilities of red cinnabar in Wilbur Springs water and in water with 10 mg/l hydrogen sulfide and 10 mg/l bisulfide. Wilbur Springs water is apparently at equilibrium with red cinnabar; the mercury content may be due to leaching of cinnabar. The other mercury concentrations found are greatly supersaturated with cinnabar; hence, the mercury cannot be ascribed to a leaching process.

TABLE 5. — *Approximate concentrations (in µg/l) of mercury species in waters at equilibrium with red cinnabar*

Dissolved Species	Temperature (°C)	
	20	100
Wilbur Springs		
$HgS(H_2S)_2$	0.1	2
$Hg(HS)_3^{-1}$	.2	
$HgS(HS)_2^{-2}$	.4	
Water with 10 mg/l H2S and 10 mg/l HS		
$HgS(H_2S)$	10^{-3}	10^{-2}
$Hg(HS_3)^{-2}$	10^{-3}	
$HgS(HS)_2^{-2}$	10^{-3}	

The mercury in solution is deposited in the immediate proximity of the springs. Algal material, sediment, hydrocarbons, sulfur from the oxidation of hydrogen sulfide in Wilbur Springs, and rocks contain relatively high concentrations of mercury (table 6).

TABLE 6. — *Mercury contents (in parts per million) of solids found in sampling localities*

	Mercury
Hydrocarbon (tarry) from the Abbott mine	500
Hydrocarbon (heavy oil) from the Wilbur oil test well	1
Fault gouge, Abbott mine	1–5
Sulfur from surface of Wilbur Springs	30

The complete removal of mercury near the springs is demonstrated by the relatively low (near or below detection limits) mercury contents in sediments and algae a few meters downstream from spring orifices. The mercury enrichment then is quite localized and does not constitute a dispersed mercury enrichment of concern to human health. Although there are local mercury enrichments, the fluids do not constitute sources of economic

mercury deposits because of the relatively large amount of rock the waters can dissolve for the volume of mercury that can precipitate.

Various calculations can be made on rates of deposition of mercury in economic deposits. Calculated using the 50-gpm discharge of Sulphur Bank reported by White and Roberson (1962) and a mercury content of 1 μg/l, the deposition of the Sulphur Bank ore would have required 40 million years, or from the Eocene to the present. However, much of the ore is deposited in Holocene rocks (White and Roberson, 1962). Our findings are in complete agreement with those of White and Roberson (1962) that the fluids presently discharging from Sulphur Bank cannot have formed the mercury deposit.

As far as we can determine, the deposition of mercury ores of economic grade is episodic. The deposition episode has ended in the area studied, although the fluids still issuing may cause the rock alteration now found. Perhaps continued detailed studies in the Coastal geochemical province will find a current depositional site to further our understanding of the geochemistry of mercury.

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