UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

USGS-OFR--79-540

DE83 902322

CHEMICAL COMPOSITION OF WATER AND GAS FROM
FIVE NEARSHORE SUBAQUEOUS SPRINGS IN CLEAR LAKE, NORTHERN CALIFORNIA

by

J. M. Thompson, J. D. Sims, Sandhya Yadav, and M. J. Rymer

U.S. Geological Survey, Menlo Park

Open-file report

79-540

This report is preliminary and has not been edited or reviewed for conformity with Geological Survey Standards and nomenclature.

Any use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

NOTICE
PORTIONS OF THIS REPORT ARE ILLEGIBLE.
It has been reproduced from the best available copy to permit the broadest possible availability.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PURCHASE ORDER NO. 03X-50540

RECEIVED 6-21-83

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTRODUCTION

In 1971 The Geysers-Clear Lake area was selected by the U.S. Geological Survey geothermal research program as a region for extensive investigation. Under this program thermal water samples were first collected in December, 1974 during a winter of normal rainfall; the last samples were collected in February, 1977 during a period of drought. The drought exposed many springs which normally are submerged by Clear Lake. The collection and analysis of these springs is reported in Thompson and others (this vol.).

Fig. 1 near here

Sims and Rymer (1976) mapped numerous springs and gas vents in Clear Lake, both along the shore and in open water. Most springs in open water are located in a linear array south of Lucern and along a line across the mouth of Konocti Bay from Wheeler Point to Fraser Point (Fig. 1). Goff and others (1976, 1977) indicate that the Konocti Bay Fault Zone terminates near Little Borax Lake. Chemical analyses of spring waters from across the mouth of Soda and Dorn bays suggest that the Konocti Bay fault zone curves westward and that these springs are an expression of the fault. Water from Kono Tayee, across the Buckingham Peninsula from Horseshoe Spring does not appear to be related to other springs along the Konocti Bay fault zone (compare Mg, Na, HCO_3 , SO_4 , and Cl in samples CLW 15 and 83).

Figure 1. Generalized map of Clear Lake and vicinity.

In 1978 another collection was made of springs from Dorn Bay (the same as Moki Beach) to Wheeler Point when two springs (Moki Beach and Riviera Beach springs) were submerged and three springs (Soda Bay, Horseshoe, and Konocti Bay springs) could be flooded by high windblown waves. The purpose of the 1978 collection was (a) to learn if any springs had changed composition significantly; (b) to test the development of a simple method of collecting water and gas from some submerged springs and gas vents mapped by Sims and Rymer (1976); and (c) to identify one or more dissolved constituents that would allow calculation of the amount of lake water dilution of the submerged spring water sample. Owing to the various collectors and changes in lake levels only three springs (LJ-78-11, 12, and 15) were positively resampled. The others are the nearest active spring to the earlier location. A special effort was made to recollect water samples from currently submerged springs which had been above lake level during the 1976 drought when the lake was at least 1 m lower than the bottom of the gage at Lakeport, California (E. J. LaCornu, oral commun., 1978).

SAMPLE COLLECTION

Samples were collected and treated using methods of Thompson (1975) and Thompson and others (1975) which are briefly summarized here. Samples from springs issuing above lake level were collected from as near the orifice as possible in a 1 liter plastic bottle attached to a 2 m aluminum pole. All but two of the samples were then decanted into a plastic filter reservoir (1 L capacity) and filtered through a 0.45 m pore size membrane filter. One aliquot was then acidified with 12 N HCl (4 mL/liter) for cation analyses of this filtered sample; another aliquot for anion analysis was not acidified. An additional 10 mL of the unfiltered spring water was transferred by pipette into 50 mL of distilled water for silica analysis. Two samples (CLW 79 and 103) were collected and filtered by use of a syringe filter system. The sample was drawn into the syringe; a 25 mm diameter filter holder containing a 0.45 m pore size membrane filter was then attached, and the sample was forced through the filter. A filtered acidified and a filtered unacidified aliquot was collected. A silica sample also was taken as described above. Samples of Clear Lake waters are "grab" samples that were not filtered.

Water samples from springs at the bottom of Clear Lake were located by feel or visual sighting of exsolved gas bubbles or by a measurable increase in temperature of the surrounding lake water. Plastic tubing was then positioned in the orifice. The tubing was completely filled with lake water before being attached to a variable rate peristaltic pump. The pump was powered by a 200 W power inverter connected to a 12 V lead-acid storage battery (Fig. 2). After approximately 10 min of pumping to thoroughly purge the tubing of lake water, the sample was collected in the plastic filter reservoir described earlier.

Fig. 2 near here.

All gas samples except the sample from the bottom of Dorn Bay were collected by the methods described by Nehring (this vol.). The Dorn Bay submerged sample was collected by a SCUBA diver who filled a funnel and tubing with lake water and placed the funnel over the spring orifice, so that gas displaced the water in the funnel. The tubing extended to a boat on the lake surface. The water remaining in the tubing was removed with a pumping syringe attached to a three way plastic stopcock. A gas collection bottle was then attached to the tubing, and the gas collected as described by Nehring (this vol.).

EQUIPMENT FOR SUBMERGED SAMPLING

Figure 2. Equipment for submerged sampling.

The funnel technique works well at Clear Lake for springs submerged in 2 or 3 m of water. At deeper locations the pressure of the overlying water column significantly compresses the gases so that the bubbles are too small to be seen under conditions of restricted visibility such as in Clear Lake. However, deep (>10 m) submerged springs are easily located using a combination of visual sightings of the expanding gas bubbles on the surface and a recording fathometer which distinguishes between the difference in density of the gas charged water and the surrounding lake water. Where underwater visibility exceeds 2-3 m, the method should be feasible to depths of ~25 m.

FIELD DETERMINATIONS

Temperatures of springs were measured using a maximum reading mercury-in-glass thermometer. The pH of the 1974 to 1977 samples was determined by pH indicator strips; a pH electrode and meter was used on the 1978 samples. Dissolved ammonia species and dissolved hydrogen sulfide species were determined spectrophotometrically with a Bausch and Lomb (B&L) "mini spec 20" and B&L NH_3 and H_2S "spectrokits".^{*/}

^{*/}

Use of brand name does not constitute a recommendation by the U.S. Geological Survey. It is for the information of the reader only.

LABORATORY DETERMINATIONS

Cations in the water sample were determined from the filtered acidified sample on all but the raw acidified 1978 lake water samples and anions from the filtered unacidified sample on all but the 1978 lake samples. Sodium, lithium, rubidium, cesium, strontium, and barium concentrations were determined by flame emission spectroscopy with excess potassium ion ($\sim 1,000$ mg/L). Potassium was measured similarly but with excess sodium ion ($\sim 1,000$ mg/L). Magnesium and calcium concentrations were determined by atomic absorption spectroscopy (AAS) with added lanthanum (1% v/v); iron, manganese, and zinc were also measured by AAS but with excess potassium ion ($\sim 1,000$ mg/L). Silica was determined as described by Shapiro and Brannock (1956) procedure except that 640 nm was used to measure the absorbance. Chloride was determined by potentiometric titration with standardized silver nitrate, a silver indicator electrode, and a double junction reference electrode. Alkalinity as bicarbonate was measured by a pH titration with standardized sulfuric acid and a combination pH electrode. The starting point of this titration is taken as the laboratory pH. Sulfate and boron were determined as described by Brown and others (1970). Fluoride was determined by an ion specific electrode using a tris buffer as described in Thompson and others (1975). In the 1978 samples fluoride was measured using a CDTA buffer as described by the manufacturer (Orion, 1977).

Gas samples were analyzed by gas chromatograph equipped with ~2 m Poropak Q and ~7 m of molecular sieves 5A columns. The sodium hydroxide solution was analyzed for CO_2 , H_2S , and NH_3 . CO_2 and H_2S were determined gravimetrically: the CO_2 by precipitation as SrCO_3 and the H_2S by precipitation as BaSO_4 after oxidization with H_2O_2 to sulfate. NH_3 was determined by an ion selective electrode. The complete procedure is described by Nehring (this vol.).

DISCUSSION

Table 1 near here.

The analytical results of the water analyses are shown in Table 1. The 1974 Big Soda Spring analysis is courtesy of R. M. Mariner (unpublished data, 1975). Because most samples collected prior to 1978 contain higher total dissolved solids than those collected in 1978, dilution by Clear Lake is assumed. Qualitatively, sulfate and ammonia concentrations indicate the amount of lake water dilution: sulfate is in the lake water; ammonia is in the spring water. Using this criteria, it appears that the sample from Dorn Bay is diluted with approximately 50% lake water. Chloride and lithium concentrations also can be used to estimate mixing proportions. Most of the springs and possibly all of them may be diluted with varying amounts of Clear Lake water (Fig. 3). The October 19, 1976 sample from Riviera Beach (CLW 103) contains 34 mg/L Cl. The Riviera Beach sample (LJ-78-13) collected in September, 1978 contains 41 mg/L Cl. Because the 1978 sample was collected using the submerged procedure we would expect its Cl concentration to be lower than the 1976 sample. Possible reasons for this are (a) the same spring was not collected; (b) dilution of the 1976 sample by wind generated waves; or (c) a real change for some unknown reason.

Table 1.--Chemical analyses of springwater along the shore of Clear Lake

	Moki Beach		Dorn Bay		Big Soda Spring		Horseshoe		Riviera Beach		Konocti Bay		Kono Tayee	Clear Lake		
Spring Name	CLW 79	LJ-78-10			GT27RM74 ¹	LJ-78-11	CLW 15	LJ-78-12	CLW 103	LJ-78-13	CLW 17	LJ-78-15	Well CLW 83	Lower Lk. CLW 58	off Lucerne LJ-78-14	nr. Anderson Is. LJ-78-16
Sample No.																
Date Collected	29 July 76	6 Sep 78	10 Sep 74	6 Sep 78	6 Dec 74	7 Sep 78	19 Oct 76	7 Sep 78	6 Dec 74	8 Sep 78	4 Dec 76	24 Jun 76	7 Sep 78	8 Sep 78		
Latitude		39°01.0'		39°00.5'		39°59.6'		38°57.5'		38°59.2'		39°02.4'	38°56.9'	39°04.8'		39°08.0'
Longitude		122 48.1'		122 47.0'		122 44.5'		122°42.2'		122°44.0'		122°45.7'	122°32.3'	122°48.3'		122°44.6'
Temp.(°C)	27	26	30.5	31	41.5	41	34	30	35	33	21.5	24	21	22		
pH	6.0	5.89	5.81	5.80	6.6	6.13	—	5.7	6.7	5.81	5.9	5.7	5.8	5.9		
1 pH	6.87	6.19	—	6.30	7.58	6.74	7.55	6.46	7.94	6.22	7.97	7.80	7.91	7.99		
Water depth (m)		—	+1	+1	—	.05	—	-.75	—	+1	—	—	—	—		
Gage height ²	.65	2.47	2.59	2.53	1.89	2.49	<0.00	2.49	1.89	2.47	—	—	1.37	2.49		2.47
SiO ₂ ³	129	83	136	137	163	159	139	104	137	133	55	6	22	21		
Fe	194	9.9	12	19	4.5	4.8	5.6	4.1	4.5	3.0	21	<.02	1.2	1.3		
Mn	.4	.26	—	.67	.21	.25	.2	.13	.23	.21	.43	<.02	<.05	<.05		
Zn	—	.13	—	.02	—	<.01	—	.97	—	<.01	.05	.04	<.01	.01		
Cu	79	60	93	89	155	138	100	69	100	83	66	24	30	26		
Mg	104	66.9	130	162	144	146	83	110	82	72	28	16	19	17		
Sr	—	.4	—	.6	—	1.0	—	.7	—	.6	—	—	.2	.3		
Ba	—	1.2	—	1.4	—	1.8	—	1.2	—	1.2	—	—	.3	.4		
Na	90	78	100	84	125	106	90	69	84	69	24	22	17	11		
K	13	5.7	13	10	21.5	13	11	6.1	13.2	8	1.6	3	2	1		
Li	.41	.22	.44	.36	.51	.47	.24	.32	.33	.27	.01	.02	.03	.03		
Ca	—	.14	.1	.18	—	.24	—	.22	—	.2	—	—	.2	.14		
Rb	—	.08	.04	.11	—	.16	—	.14	—	.12	—	—	.1	.09		
NH ₄	—	2.4	1.9	3.6	—	2.0	—	1.9	—	.9	—	—	<.1	<.1		
HCO ₃	936	611	1190	1090	1310	1420	923	852	775	693	306	232	160	162		
SO ₄	1	7	1	2	1	1	1	1	<.5	2	31	11	11	11		
Cl	59	36	66	65	78	76	34	41	48	44	7.3	3	4	4		
F	.11	.2	.3	.45	.37	<.1	.2	.32	.5	<.1	.21	.15	<.1	.11		
B	13	10.3	15	12.5	19	15.3	13	9	9	6.5	5.3	1.6	.65	.75		
H ₂ S	—	<0.0	—	<0.0	—	<0.0	—	<0.0	—	<0.0	—	—	—	—		

¹ R. M. Mariner, unpublished data, 1975.² At Lakeport gage.³ All analyses in mg/L.

Fig. 3 near here. Table 2 near here.

The gas compositions of the various springs are shown in Table 2. Two gas analyses from Nehring (this vol.) are also listed. The two gas samples from Dorn Bay reveal the influence of the surrounding lake water. The nitrogen and oxygen concentrations in the surface sample are greater than in the bottom sample; furthermore the $N_2:O_2$ in the surface sample is 3.97 and is 7.17 in the bottom sample. We interpret this difference in the $N_2:O_2$ as resulting from contamination of the rising gas by air that exsolves from overlying water as the gas passes through it. This same situation is illustrated in the gas from the Shag Rock locality. The surface sample contains 30.1 mole % air gases. Unfortunately, owing to limited visibility (41 m) on the bottom and small size of the escaping gas bubbles, no bottom sample was collected at Shag Rock. It would be interesting to correlate the amount of air gases in surface gas sample of springs or vents with depth of overlying water and the amount of air gases in the bottom sample with bottom depth. Unfortunately, with only two samples, the results here are statistically meaningless.

Figure 3. Plot of lithium vs chloride

Table 2.—Chemical analyses of spring gases along the shore of Clear Lake

Name	Dorn Bay		Moki Beach	Soda Bay	Horseshoe Spring	Riviera Beach	Konoceti Bay		Shag Rock
Sample #	Surface	Bottom	=====	LJ-78-11	LJ-78-12	LJ-78-13	LJ-78-15	=====	LJ-78-17
Date	6 Sep 78	6 Sep 78	=====	6 Sep 78	7 Sep 78	7 Sep 78	8 Sep 78	=====	
Depth	0.00	-2.0	=====	+.1m	+.05m	-.75m	+.1	=====	-.05
CO ₂	90.45	96.13	99.23	99.79	99.57	94.73	87.02	94.76	64.73
H ₂ S	<.000	<.000	<.000	<.000	<.000	<.000	<.000	<.000	<.000
NH ₃	.023	.0064	—	.0119	<.000	.0235	.0282	—	.304
He	<.000	<.000	<.000	<.000	<.000	<.000	<.000	<.000	<.000
N ₂	4.58 x 10 ⁻⁵	<.000	2.5 x 10 ⁻⁵	3.55 x 10 ⁻⁵	2.19 x 10 ⁻⁴	<.000	<.000	<.000	<.000
Ar	.058	.0282	.0033	6.44 x 10 ⁻⁴	.0016	.0490	.0688	.025	.386
O ₂	.634	.0749	.0047	.011	.0271	.132	.124	.041	6.34
N ₂	2.52	.537	.13	.0485	.124	1.16	4.45	1.48	23.8
CH ₄	5.77	3.02	.63	.104	.189	3.45	7.01	3.76	<.000
C ₂ H ₆	<.000	<.000	—	<.000	<.000	<.000	<.000	—	<.000
Total	99.45	99.79	100.70	99.92	99.91	99.54	98.71	100.07	99.50

Volumes in Mole %
Analyses by M. Mehrling, USGS

CONCLUSIONS

We have demonstrated that gas and water samples can be collected from shallow submerged springs relatively simply using a peristaltic, battery powered pump. Qualitatively sulfate, ammonia, chloride and lithium concentrations may be used to estimate the amount of lake water contamination. Our gas sampling technique, using an inverted funnel and long tube to the surface only where visibility was greater than 2-3 m. Analyses of near surface compared to deeper submerged gas indicates air contamination in the near surface sample. Thus gas samples should be collected deep underwater or as near the spring vent or gas orifice as possible.

REFERENCES

- Brown, Eugene, Skougstad, M. W., and Fishman, M. D., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water Resources Investigations, Book 5, Chapter A1, 160 p.
- Goff, F. E., Donnelly, J. M., Thompson, J. M., and Hearn, B. C., Jr., 1976, The Konocti Bay fault zone, California: Potential areas for geothermal exploration (abs.): Geological Society of America Abstracts with Programs, v. 8, no. 3, p. 375-376.
- Goff, F. E., Donnelly, J. M., Thompson, J. M., and Hearn, C. B., Jr., 1977, Geothermal prospecting in The Geysers-Clear Lake area, northern California: Geology, v. 5, p. 509-515.
- Nehring, N. L., 1979, Gases from springs and wells in the Clear Lake-Geysers area of northern California: this volume, p.
- Orion, 1977, Fluoride electrode instruction manual, p. 2-3.
- Shapiro, Leonard, and Brannock, W. W., 1956, Rapid analysis of silicate rocks: U.S. Geological Survey Bulletin 1036C, p. 32-33.
- Sims, J. D., and Rymer, M. J., 1976, Map of gaseous springs and associated faults in Clear Lake, California: U.S. Geological Survey Map MF-721.
- Thompson, J. M., 1975, Selecting and collecting thermal springs for chemical analysis: A method for field personnel: U. S. Geological Survey Open-File Report 75-68, 12 p.

Thompson, J. M., Goff, F. E., and Donnelly, J. M., 1979, Chemical analyses of waters from springs and wells from the Clear Lake volcanic area, northern California: this volume.

Thompson, J. M., Presser, T. S., Barnes, R. B., and Bird, D. B., 1975, Chemical analyses of the waters of Yellowstone National Park, Wyoming, 1966-1973: U.S. Geological Survey Open-File Report 75-25, 59 p.

Figure Captions

Figure 1. Generalized map of Clear Lake and vicinity.

Figure 2. Equipment for submerged sampling.

Figure 3. Plot of Lithium vs chloride.