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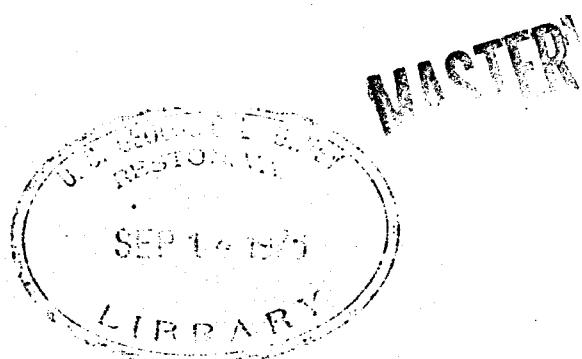
CHEMICAL CHARACTERISTICS

OF THE MAJOR THERMAL SPRINGS

OF MONTANA

By R. H. Mariner, T. S. ⁶ Presser, and W. C. ⁰ Evans

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ABSTRACT

Twenty-one thermal springs in western Montana were sampled for chemical, isotope, and gas compositions. Most of the springs issue dilute to slightly saline sodium-bicarbonate waters of neutral to slightly alkaline pH. A few of the springs issue sodium-mixed anion waters of near neutral pH. Fluoride concentrations are high in most of the thermal waters, up to 18 milligrams per litre, while F/Cl ratios range from 3/1 in the dilute waters to 1/10 in the slightly saline waters. Most of the springs are theoretically in thermodynamic equilibrium with respect to calcite and fluorite. Nitrogen is the major gas escaping from most of the hot springs; however, Hunters Hot Springs issue principally methane. The deuterium content of the hot spring waters is typical of meteoric water in western Montana.

Geothermal calculations based on silica concentrations and Na-K-Ca ratios indicate that most of the springs are associated with low temperature aquifers (less than 100°C). Chalcedony may be controlling the silica concentrations in these low temperature aquifers even in "granitic" terranes.

INTRODUCTION

Most of the thermal springs in Montana are located in the southwestern part of the State. This is an area of complex geologic structure with numerous folds and faults associated with intrusive and extrusive igneous rocks. The principal geologic features of this part of Montana are the Cretaceous through early Tertiary batholiths such as Idaho, Boulder, Tobacco Root, and Philipsburg. Extensive rhyolite flows and related lacustrine deposits of Middle Tertiary age are associated with most of the batholiths. The extensive volcanic rocks adjacent to Yellowstone Park are also of Middle Tertiary age. The last volcanic activity in the State occurred in the late Tertiary (Miocene and Pliocene) with the eruption of small quantities of basalt. Perry (1962) gives a more complete review of Montana's geologic history.

Waring (1965) lists 40 thermal springs in Montana, none of which issue at boiling temperatures. We have sampled 21 of the hot springs for detailed chemical analysis including stable isotopes and gases. The sampled hot springs all issue at temperatures of more than 100°F (38°C). Most of the springs have been utilized by resorts, although some of the resorts are not currently active. Four KGRA's (Known Geothermal Resource Areas) have been designated in the State (Godwin and others, 1971): Corwin Springs, Boulder Hot Springs, Yellowstone, and the hot well at Marysville.

Some geothermal sampling has been carried out in the State by Montana State University. Chadwick and Kaczmarek (1975) present major cation and silica analyses for many of Montana's hot springs. Their paper makes available data collected by Kaczmarek (1974) as part of a Master's thesis on geothermometry of selected Montana hot spring waters. A U.S. Geological Survey open-file report (Taylor and Hinds, 1976) contains a partial analysis of water collected from La Duke Hot Spring.

The purpose of our sampling was to obtain complete chemical analyses of water collected from the major hot springs in Montana. These data were used to estimate aquifer temperatures, thereby indicating where additional detailed work would be necessary to determine Montana's geothermal potential. Arbitrarily, it was decided to limit our sampling to hot springs which issued at temperatures of more than 38°C. This arbitrary temperature (38°C) was chosen because it is roughly the temperature used to separate hot springs from warm springs (Meizner, 1923).

METHODS AND PROCEDURES

Water collected at points as close to the orifices of the springs or wells as possible was immediately pressure-filtered through a 0.1 μm (micrometre) membrane filter using compressed nitrogen as the

pressure source. Filtered water samples were stored in plastic bottles which had been acid-washed to remove contaminants prior to use. Samples for heavy metal analyses were immediately acidified with concentrated nitric acid to a pH of 2 or less to insure that the metals would remain in solution. Samples collected for Group II metals were acidified with concentrated hydrochloric acid to pH 2. Ten millilitres of filtered sample were diluted to 100 millilitres with distilled deionized water to slow the polymerization of silica. Three samples of unfiltered untreated water were collected in 125-ml (millilitre) glass bottles with polyseal caps for stable isotope analysis. Samples of any gases escaping from the spring were collected in gas-tight glass syringes which were placed in a bottle of the native water for transport back to the laboratory.

Field determinations were made of barometric pressure, air temperature, water temperature, pH, alkalinity, ammonia, and sulfide. Extraction of aluminum and preservation of mercury were also performed in the field. Water temperatures were determined with a thermistor probe and a maximum reading mercury-in-glass thermometer. Detailed descriptions of our sampling techniques are given in Presser and Barnes (1974). Alkalinity was measured immediately after the sample was withdrawn from the spring. Sulfide (total sulfides as H_2S) was precipitated as zinc sulfide from the hot sample and titrated by the iodometric method described by Brown, Skougstad, and Fishman (1970). Mercury was stabilized for later analysis in the laboratory by addition of 2:1 $H_2SO_4:HNO_3$, 5 percent $KMnO_4$ (W/V), and 5 percent $K_2S_2O_8$ (W/V). Ammonia was determined by allowing the thermal spring sample to cool to ambient temperature, adding sodium hydroxide to raise the pH to approximately 12, and measuring the dissolved ammonia with an ammonia-specific ion electrode. Water samples for aluminum were complexed with 8-hydroxyquinoline, buffered at pH 8.3, and extracted with methyl isobutyl ketone in the field as described by Barnes (1975).

Silica, sodium, potassium, lithium, rubidium, cesium, calcium, magnesium, cadmium, cobalt, copper, iron, nickel, lead, manganese, and zinc were determined by direct aspiration on a double beam atomic absorption (A. A.) spectrophotometer in our laboratory. Detection limits in micrograms per litre ($\mu g/l$) for the direct aspiration of solutions containing the heavy metals on our instrument are cadmium (10), cobalt (50), copper (10), iron (20), nickel (20), lead (100), manganese (20), and zinc (10). Boron was determined in our laboratory by either the Dianthrimide method or the Carmine method (Brown and others, 1970), depending on the concentration range. Fluoride was determined in our laboratory by specific ion electrode using the method of R. B. Barnes (written commun., 1973). Chloride and sulfate were determined by the Mohr and Thorin methods, respectively, as described by Brown, Skougstad, and Fishman (1970). Specific conductances were determined by a direct reading instrument in the laboratory at 25°C.

Mercury was determined by a flameless atomic absorption technique (Environmental Protection Agency, 1971). The organic extract containing the aluminum complex was analyzed by A. A.

The CO_2 -equilibration method of Cohn and Urey (1938) and the uranium technique of Bigeleisen and others (1952) were used in the analysis for oxygen and deuterium isotope ratios in the water samples. Isotopic ratios of $^{18}\text{O}/^{16}\text{O}$ and D/H were measured mass spectrometrically.

Gases were analyzed by gas chromatography as soon as possible after returning to the laboratory, always within two weeks of the date of sample collection. Linde Molecular Sieve 13X was used to separate and quantify $(\text{O}_2 + \text{Ar})$, N_2 , and CH_4 , while Porapak Q was used for CH_4 and CO_2 . The columns were run at room temperature with helium as the carrier gas. The gases were detected by thermal conductivity.

SAMPLE-SITE SELECTION

Selection of sample sites was based largely on the compilation of Waring (1965). Sampling was arbitrarily restricted to thermal springs which issued at temperatures of more than 38°C .

Table 1 contains the names, location, and a brief description of the sampled thermal springs and wells. Spring names were taken from U.S. Geological Survey topographic maps. Figure 1 shows the distribution of the thermal springs and wells covered in this report.

WATER CHEMISTRY

Most of the hot spring waters are relatively dilute; only three spring waters contain enough dissolved solids to be considered slightly saline, 1,000 to 3,000 milligrams per litre (mg/l) dissolved solids (table 2). These slightly saline waters, New Biltmore Hot Spring, White Sulphur Spring, and Warm Springs have the lowest pH's of any of the hot springs, 6.76, 6.49, and 6.46, respectively. Generally, among Montana's hot springs, waters with higher total dissolved solids have lower pH's.

Sodium is the major cation in all of the spring waters except La Duke, Chico, and New Biltmore hot springs. La Duke and Chico issue Ca-Na waters while New Biltmore issues a Ca water. The principal anion is either HCO_3 (12 springs) or SO_4 (6 springs) except at Pipestone, Broadwater, and Bozeman hot springs where SO_4 and HCO_3 exist in approximately equal amounts. Fluoride is present in larger molal concentration than chloride in 10 of the sampled hot springs. White Sulphur Springs is highest in lithium (1.3 mg/l) and boron (9.1 mg/l). Ammonia was detected at concentrations of more than 1 mg/l at White Sulphur Springs (2.1 mg/l).

Table 1.--Location and description of sampled springs

Springs	Location and date of collection	Description
Jardine (Jackson) Hot Springs-----	T. 5 S., R. 15 W. Aug. 16, 1974	Beaverhead County
		Springs issue 250 metres east of the town of Jackson; very gassy springs; aggregate flow at least 1,000 lpm; inactive resort; Tertiary sedimentary rocks overlying Belt Supergroup.
Elkhorn Hot Springs-----	NE $\frac{1}{4}$ sec. 29, T. 4 S., R. 12 W. Aug. 20, 1974	Four springs and several seeps; 400 lpm; no gas; granite; water used in swimming pool.
Gregson (Fairmont) Hot Springs-----	NW $\frac{1}{4}$ sec. 2, T. 3 N., R. 10 W. Aug. 19, 1974	Deer Lodge County
		Extensive resort development; springs issue in concrete-lined pools and covered concrete tanks; sporadic gas discharge; large flow (probably 1,000 lpm); Quaternary fill and Tertiary volcanic rocks overlying granite.
Warm Springs (State Hospital)-----	NE $\frac{1}{4}$ sec. 24, T. 5 N., R. 10 W. Aug. 19, 1974	Springs issue in the top of a large carbonate mound; some gas but impossible to collect because of grill cover; sample from outflow pipe at south side of hill; large flow (est. 600 lpm).
Bozeman Hot Springs-----	E $\frac{1}{4}$ sec. 14, T. 2 S., R. 4 E. Aug. 25, 1974	Gallatin County
		Springs no longer active; sample from a well used by swimming pool resort; thick alluvium and Tertiary fill.
Alhambra Hot Springs-----	NE $\frac{1}{4}$ sec. 16, T. 8 N., R. 3 W. Aug. 23, 1974	Jefferson County
		Numerous small carbonate mounds; sample from galvanized pipe leading from enclosed spring to residence swimming pool; granite bedrock; estimated flow 40 lpm.
Boulder Hot Springs (A)-----	SW $\frac{1}{4}$ sec. 10, T. 5 N., R. 4 W. (B)-----	Springs issue in concrete tank near swimming pool; large but indeterminate flow rate; granite bedrock; A--open stand pipe southeast of hotel, B--round concrete tank behind hotel.
Pipestone Hot Springs-----	T. 2 N., R. 5 W. Aug. 18, 1974	Principal spring issues under some artesian pressure through a two-inch pipe on the west side of the creek; estimated flow 300 lpm; inactive resort; alluvium overlying granite.
Broadwater Hot Springs-----	NE $\frac{1}{4}$ sec. 28, T. 10 N., R. 4 W. Aug. 24, 1974	Lewis and Clark County
		Springs issue in covered pits; very low flow rate (<50 lpm); closed resort.
Norris Hot Springs-----	E $\frac{1}{4}$ sec. 14, T. 3 S., R. 1 W. Aug. 21, 1974	Madison County
		Principal springs issue in plank-lined swimming pool; discharge estimated at 400 lpm; numerous springs and seeps; campground; Precambrian gneiss; almost constant gas discharge.
Potosi Hot Springs-----	Unsurveyed 45°36'N by 111°54'W. Aug. 21, 1974	Original springs dynamited, water taken from stream which issues from the rubble pile; granite bedrock and Tertiary volcanic rocks; flow at least several hundred litres per minute.

Table 1.--Location and description of sampled springs--Continued

Springs	Location and date of collection	Description
Madison County--Continued		
Silver Star Hot Springs-----	SW $\frac{1}{4}$ sec. 1, T. 2 S., R. 6 W. Aug. 18, 1974	Springs issue in rock-lined tanks; sporadic gas discharge; water used in swimming pool; estimated flow 150 lpm; Tertiary lake sediments overlying granite.
New Biltmore Hot Springs-----	N $\frac{1}{4}$ sec. 28, T. 4 S., R. 7 W. Aug. 17, 1974	Springs issue in covered concrete tanks; water used in swimming pool; flow rate indeterminate but probably more than 100 lpm.
Meagher County		
White Sulphur Springs-----	T. 9 N., R. 6 E.	Springs issue in concrete tanks; sporadic gas; high flow rate (1,500-2,000 lpm); film of sulfur on the water surface; motel swimming pool; Tertiary lake deposits overlying Belt Supergroup.
Missoula County		
Lolo Hot Springs-----	T. 11 N., R. 23 W.	Springs issue in concrete tanks; no gas; flow approximately 100 lpm; swimming pool and camping facility; granite bedrock.
Park County		
Chico Hot Springs-----	SW $\frac{1}{4}$ sec. 1, T. 6 S., R. 8 E. Aug. 25, 1974	Several covered springs; flow more than 500 lpm; water used in resort swimming pool; Tertiary basalts overlying Precambrian rocks.
La Duke Hot Springs (A)----- (B)-----	SW $\frac{1}{4}$ sec. 32, T. 8 S., R. 8 E. July 2, 1975	Principal springs issue in long concrete tank beside road; 500 lpm; numerous small seeps; some carbonate precipitate; Tertiary basalts overlying Precambrian; A--concrete tank, B--seep spring in road cut south of tank.
Hunters Hot Springs (A)----- (B)----- (C)-----	SW $\frac{1}{4}$ sec. 9, T. 1 S., R. 12 E. July 2, 1975	Three principal springs within 150 metres of one another; high flow rate 5,000 lpm; sporadic gas discharge; inactive resort; springs issue in concrete tanks; Cretaceous to Paleocene sedimentary rocks; spring A--southernmost, B--middle, C--northernmost spring south of road.
Ravalli County		
Medicine Springs-----	T. 1 N., R. 20 W. Aug. 16, 1974	Springs used in swimming pool and campground; flow estimate 400 lpm; no gas; granite bedrock; water sample from small nonenclosed spring southwest side of complex.
Sleeping Child Hot Springs (A)----- (B)-----	Unsurveyed 46°5'N by 114°0'W. Aug. 15, 1974	Two springs about 150 metres apart, aggregate flow probably more than 2,000 lpm; swimming pool; gneiss bedrock; A--spring at base of cliff north of pool; B--spring up the creek northeast of the pool.
Sanders County		
Camas Hot Springs-----	sec. 3, T. 21 N., R. 24 W. July 3, 1975	Several springs issuing in large concrete tanks; at least several hundred litres per minute; sporadic gas discharge; granite bedrock.

MONTANA

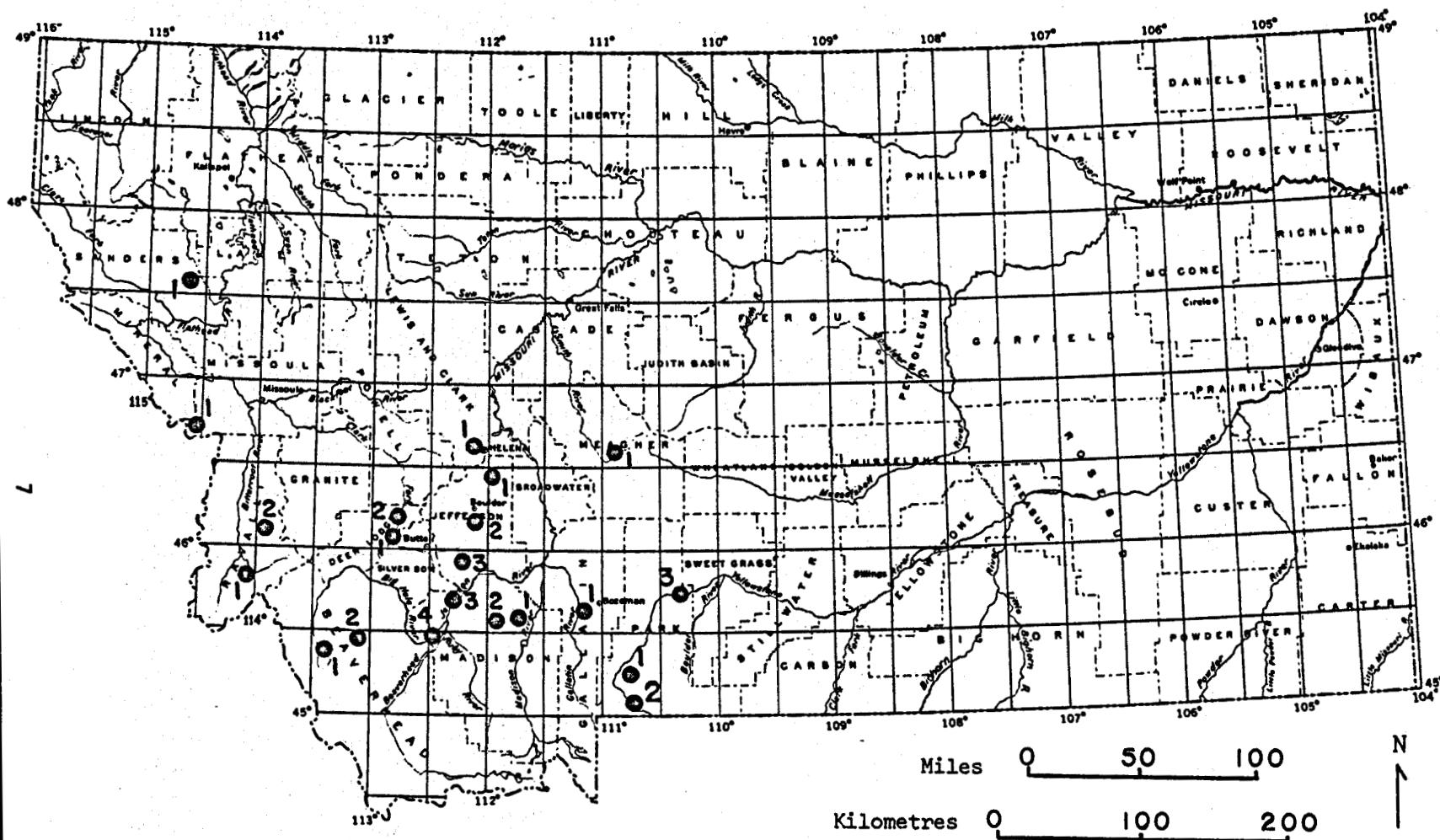


Figure 1. Map of the State of Montana showing the location of the sampled thermal springs.

The numbered dots correspond to sampled springs listed by county in the tables.

Table 2.--Major element chemical composition
[Concentrations are in milligrams per litre; dashes indicate the absence of data]

Spring name	Temperature (°C)	pH	Specific conductance (micromhos)	Silica (SiO ₂)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Lithium (Li)	Alkalinity (as HCO ₃) ₁	Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Boron (B)	Dissolved ² / constituents
Beaverhead County															
Jardine (Jackson) Hot Springs----	58	6.77	972	52	10	3.7	240	10	0.32	614	45	7.7	2.0	0.83	986
Elkhorn Hot Springs-----	48½	8.94	209	55	1.9	<0.1	48	0.7	.05	85	27	1.7	2.6	.04	222
Deer Lodge County															
Gregson (Fairmont) Hot Springs---	70	8.41	761	85	3.9	<.1	165	3.9	.64	166	180	17	18	.30	640
Warm Springs (State Hospital)----	77	6.46	1,510	56	220	22	120	26	.36	258	670	5.0	3.9	.10	1,310
Gallatin County															
Bozeman Hot Springs-----	50	8.58	624	66	9.5	2.7	120	2.8	.04	132	110	46	9.2	.20	498
Jefferson County															
Alhambra Hot Spring-----	56½	7.23	929	66	18	3.5	220	9.5	.32	484	89	10	8.4	.24	909
Boulder Hot Springs (A)-----	62	8.52	525	106	2.7	<.1	120	3.8	.22	171	74	19	11	.54	508
(B)-----	76	8.50	523	108	2.2	<.1	120	3.8	.24	168	74	19	11	.56	507
Pipestone Hot Springs-----	57	8.72	455	66	2.6	<.1	98	1.9	.09	108	94	20	5.3	.28	396
Lewis and Clark County															
Broadwater Hot Springs-----	62	8.53	796	98	11	.9	165	5.8	.48	218	170	33	9.4	.80	712
Madison County															
Norris Hot Springs-----	52½	7.58	903	88	17	3.2	180	10	.09	380	130	23	7.4	.10	839
Potosi Hot Springs-----	49½	8.63	471	46	10	<.1	91	1.6	.05	67	140	5.9	6.2	<.02	368
Silver Star Hot Springs-----	71½	8.17	808	110	9.3	.3	170	6.4	.34	170	190	31	8.7	.25	696
New Biltmore Hot Springs-----	53	6.76	2,160	46	290	73	160	24	.18	226	1,100	46	3.3	.92	1,969
Meagher County															
White Sulphur Springs-----	46	3/6.8	2,220	51	44	12	480	20	1.3	835	310	180	7.4	9.1	1,950

Table 2--Major element chemical composition--Continued

Spring name	Temperature (°C)	pH	Specific conductance (micromhos)	Silica (SiO ₂)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Lithium (Li)	Alkalinity ^{1/} (as HCO ₃) ^{1/}	Sulfate (SO ₄)	Chloride (Cl)	Fluoride (F)	Boron (B)	Dissolved ^{2/} constituents
Missoula County															
Lolo Hot Springs-----	44	9.27	225	72	1.8	<0.1	52	1.2	0.03	86	18	6.1	6.4	0.11	244
Park County															
Chico Hot Springs-----	42	7.38	379	34	35	8.8	35	6.8	.03	170	41	10	.9	.06	342
La Duke Hot Springs (A)-----	65	6.52	2,460	49	320	58	230	23	.24	297	1,200	45	3.6	.46	2,226
(B)-----	65	6.28	2,420	48	310	57	230	23	.26	329	1,200	45	3.6	.49	2,246
Hunters Hot Springs (A)-----	60	9.13	354	65	.9	<.1	85	.6	.03	197	4/11	18	5.6	.67	384
(B)-----	57	8.82	357	64	.8	<.1	85	.6	.03	194	4/10	19	5.6	.73	380
(C)-----	60	---	359	65	.7	<.1	88	.6	.03	---	4/18	16	5.6	.72	---
Ravalli County															
Medicine Springs-----	45	8.59	343	60	1.9	<.1	80	1.4	.20	125	33	6.7	14	.12	322
Sleeping Child Hot Springs (A)---	52	8.20	538	66	5.4	<.1	120	2.9	.18	170	87	9.5	15	.35	476
(B)---	43	8.11	505	60	6.2	.2	110	2.6	.17	162	81	8.8	14	.33	445
Sanders County															
Camas Hot Springs-----	45	9.39	367	70	.9	<.1	85	1.7	.04	189	4/38	8.5	5.6	.34	399

^{1/}Total alkalinity as bicarbonate.^{2/}Dissolved constituents are a total of the major element concentrations in milligrams per litre.^{3/}pH approximate due to meter instability.^{4/}Not corrected for oxidation of sulfide to sulfate.

and Camas Hot Springs (3.0 mg/l). Cesium was found in detectable amounts (0.1 mg/l) at Gregson, Warm Springs, Broadwater, and White Sulphur Springs. Aluminum concentrations were highest in dilute waters, decreasing in the more concentrated waters.

Detectable amounts of nickel (20 $\mu\text{g/l}$) were found at La Duke, New Biltmore, and Warm Springs. Mercury concentrations were at or below the detection limits (0.1 $\mu\text{g/l}$) in all of the spring waters. Iron concentrations of more than 0.02 mg/l were found in some of the more concentrated waters: New Biltmore (0.10 mg/l), White Sulphur (0.11 mg/l), Broadwater (0.07 mg/l), La Duke-B (0.07 mg/l), and Warm Springs (0.05 mg/l). Zinc was the only heavy metal to be widely distributed (table 3). However, the apparent abundance of zinc may be due to contamination by manmade materials thrown into the springs. Detectable amounts of cadmium, cobalt, copper, and lead were not found in any of the spring waters. Compositions of several fresh waters are listed in table 4.

Molal ratios (table 5) of K/Na and $\sqrt{\text{Ca}}/\text{Na}$ are very similar except for La Duke, Chico, New Biltmore, and Warm Springs. Most of the springs have ratios of K/Na ranging from 0.01 to 0.03 and $\sqrt{\text{Ca}}/\text{Na}$ ratios ranging from 1 to 4. La Duke, Chico, New Biltmore, and Warm Springs have higher K/Na ratios (0.06, 0.11, 0.09, and 0.13) and higher $\sqrt{\text{Ca}}/\text{Na}$ ratios (8.9, 19, 12, and 14), respectively. The higher K/Na and $\sqrt{\text{Ca}}/\text{Na}$ ratios at La Duke, Chico, New Biltmore, and Warm Springs may be due to water interaction with basaltic rocks or calcareous sediments while the other spring waters issue from granitic rocks. Dilute thermal spring waters have the largest ratios of F/Cl (3/1) while more concentrated waters have the smallest ratios (0.1/1).

GAS COMPOSITIONS

The gas escaping from six of the hot springs consists essentially of nitrogen (table 6), with only Jardine Hot Spring containing appreciable carbon dioxide (16 percent). Bodvarsson (1961) has shown that gases associated with the lower temperature thermal waters of Iceland are principally nitrogen. Gases collected from thermal springs associated with higher temperature thermal systems are typically rich in carbon dioxide (Ellis, 1970). Hunters and Camas hot springs release appreciable methane, 64 and 8 percent, respectively. Gas collected from White Sulphur Springs was not analyzed due to failure of the gas syringe; however, the theoretical PCO_2 for this water is higher than for Jardine.

MINERAL EQUILIBRIUM

Solution-mineral equilibrium calculations using the computer program SOLMNEQ (Kharaka and Barnes, 1973) indicate that most of the hot springs

Table 3.--Trace element chemical composition
 [Concentrations are in milligrams per litre; dashes indicate the absence of data]

Table 3.--Trace element chemical composition--Continued

Spring name	Hydrogen sulfide (H ₂ S)	Aluminum (Al)	Rubidium (Rb)	Ammonia (as N)	Manganese (Mn)	Zinc (Zn)
Meagher County						
White Sulphur Spring-----	0.7	0.006	0.09	2.1	0.15	0.02
Missoula County						
Lolo Hot Springs-----	<.5	.010	<.02	<.1	<.02	.01
Park County						
Chico Hot Springs-----	.6	---	<.02	<.1	<.02	.01
La Duke Hot Springs (A)-----	<1	<.001	.07	0.22	.02	<.01
(B)-----	<1	---	.07	---	<.02	.01
Hunters Hot Springs (A)-----	5.3	0.040	<.02	.16	<.02	<.01
(B)-----	---	---	<.02	---	<.02	.05
(C)-----	---	---	<.02	---	---	---
Ravalli County						
Medicine Springs	0.6	0.007	<0.02	<0.1	<0.02	<0.01
Sleeping Child Hot Springs (A)-----	.8	.004	<.04	<.1	<.02	<.01
(B)-----	<1	---	.03	---	<.02	<.01
Sanders County						
Camas Hot Springs-----	7.4	.021	<.02	3.0	<.02	<.01

Table 4.--Chemical composition of selected fresh waters in Montana
 [Chemical concentrations are in milligrams per litre]

Sample	Location	Temperature (°C)	pH	Specific conductance (micromhos at 25°C)	Silica (SiO ₂)	Sodium (Na) ^{1/}	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Alkalinity (as HCO ₃)	Chloride (Cl)	Sulfate (SO ₄)	Fluoride (F)	Boron (B)
Unnamed creek	Near Lolo Hot Spring	10	7.31	45	18	2.5	0.8	4.8	1.3	26	0.3	<1	<0.1	<0.02
Unnamed creek	Near Sleeping Child Hot Springs	10	7.32	48	19	3.0	1.5	5.0	1.1	27	.4	2	<.1	<.02
Unnamed creek	Near Medicine Hot Spring	8	7.64	79	14	2.9	.6	11	1.1	45	.2	2	.1	<.02
Unnamed creek	Near Jardine Hot Springs	13	8.04	67	16	5.1	.8	6.0	1.8	36	1.2	2	<.1	.03
Big Hole River	Near New Biltmore Hot Springs W 1/2 sec. 28, T. 4S., R. 12W.	14	7.36	220	14	8.4	2.6	27	6.6	104	2.1	14	.2	.03
South Fork Hot Springs Creek	Near Elkhorn Hot Springs NE 1/4 NE 1/4 sec. 29, T. 4S., R. 12W.	8	6.78	81	27	5.7	1.9	7.0	1.4	19	1.1	18	<.1	.03
Unnamed spring	Near Norris Hot Spring NW 1/4 sec. 13, T. 3S., R. 1W.	14	7.68	322	32	21	3.7	34	10	154	7.6	27	.7	.04

^{1/} Lithium concentrations less than 0.02 milligrams per litre in all samples.

Table 5.--Molal ratios of K/Na, $\sqrt{\text{Ca}/\text{Na}}$, F/Cl, and B/Cl in Montana thermal spring waters

Table 5.--Molal ratios of K/Na, \sqrt{Ca}/Na , F/Cl, and B/Cl in Montana thermal spring waters--Continued

Springs	K/Na	\sqrt{Ca}/Na	F/Cl	B/Cl
Park County				
Chico Hot Springs-----	0.11	19	0.17	0.019
La Duke Hot Springs (A)-----	.059	8.9	.15	.034
(B)-----	.059	8.8	.15	.036
Hunters Hot Springs (A)-----	.0042	1.3	.58	.12
(B)-----	.0042	1.2	.55	.13
Ravalli County				
Medicine Springs-----	.010	2.0	3.9	.059
Sleeping Child Hot Springs (A)-----	.014	2.2	3.0	.12
(B) -----	.014	2.6	3.0	.12
Sanders County				
Camas Hot Springs-----	.018	1.3	1.3	.13

Table 6.--Compositions of gases escaping from thermal springs
 [Composition is in volume percent]

1/ No detectable ethane.

are in equilibrium with or are slightly supersaturated with respect to calcium carbonate (calcite or aragonite), fluorite, and silica phases (alpha-cristobalite or chalcedony), table 7. Equilibrium calculations should be considered when chemical geothermometers are calculated because precipitation of calcium phases or equilibrium with silica phases other than quartz can lead to erroneous estimates of subsurface temperatures.

A plot of the free energy of formation for calcite and fluorite at the spring temperatures as a function of the total dissolved constituents, figure 2, shows that the more dilute waters are generally unsaturated with these minerals while the more concentrated waters are generally at equilibrium with calcite and fluorite. Theoretical equilibrium with respect to calcite and fluorite is generally observed above 370 and 480 mg/l dissolved constituents, respectively. Waters which are unsaturated with respect to calcite and fluorite could have several origins: (1) insufficient water-rock reaction could have occurred to attain equilibrium with these minerals, (2) a water in equilibrium with these minerals could have been diluted with a fresh water, (3) a decrease in temperature without dilution could result in unsaturation because both minerals are more soluble at lower temperatures, or (4) the country rock might be exceptionally low in calcium or fluoride. Calcite equilibrium is very susceptible to changes in pH. Loss of carbon dioxide from a water in equilibrium with calcite would result in the water becoming supersaturated with respect to calcite. Subsequent precipitation of calcite would lead to unsaturation with respect to fluorite provided the water was in equilibrium with fluorite before the pH changed. Conversely, a pH decrease could be brought about by redissolving carbon dioxide "boiled off" of a geothermal fluid at depth in cooler waters encountered near the surface. Spring waters which are in equilibrium with both calcite and fluorite at the spring temperature may be essentially unchanged in temperature, pH, and total concentration relative to values for these variables at depth. However, the observation that a water is theoretically in thermodynamic equilibrium with calcite and(or) fluorite at the measured spring temperature may also indicate that the water has re-equilibrated with calcite and fluorite at that temperature. Thus, supersaturation, equilibrium, or unsaturation with respect to calcite and fluorite does not prove dilution, carbon dioxide loss or gain, or temperature changes.

The combination of supersaturation with respect to calcite and unsaturation with respect to fluorite at Silver Star and Broadwater hot springs probably indicates that some calcium has been precipitated from the water as calcium carbonate. In contrast, the water at Bozeman Hot Springs is supersaturated with respect to calcite but is in equilibrium with fluorite and has not yet lost appreciable amounts of calcium. Possible explanations for the negative free energies of formation for calcite and fluorite observed at Jardine Hot Springs include dilution

Table 7.--States of reactions with respect to calcite, aragonite, chalcedony, alpha-cristobalite and fluorite

Spring name	ΔG (kcal)				
	Calcite	Aragonite	Chalcedony	Alpha-cristobalite	Fluorite
Beaverhead County					
Jardine (Jackson) Hot Springs-----	-1.02	-1.11	+0.23	-0.06	-1.50
Elkhorn Hot Springs-----	.37	-.44	.16	-.12	-1.70
Deer Lodge County					
Gregson (Fairmont) Hot Springs-----	+.12	+.04	+.27	-.03	.00
Warm Springs (State Hospital)-----	+.06	-.06	+.02	-.28	+.20
Gallatin County					
Bozeman Hot Springs-----	+.49	+.42	+.37	+.09	-.04
Jefferson County					
Alhambra Hot Springs-----	-.12	-.20	+.40	+.11	+.05
Boulder Hot Springs (A)-----	+.00	-.09	+.54	+.24	-.48
(B)-----	+.07	-.04	+.32	+.02	-.62
Pipestone Hot Springs-----	-.18	-.26	+.21	-.08	-1.10
Lewis and Clark County					
Broadwater Hot Springs-----	+1.00	+.90	+.45	+.16	-.10
Madison County					
Norris Hot Springs-----	+.15	+.07	+.63	+.34	-.06
Potosi Hot Springs-----	+.13	+.05	+.13	-.15	-.33
Silver Star Hot Springs-----	+.45	+.35	+.48	+.18	-.26
New Biltmore Hot Springs -----	+.07	-.01	+.22	-.06	+.15

Table 7.--States of reactions with respect to calcite, aragonite, chalcedony, alpha-cristobalite and fluorite--Continued

Spring name	ΔG (kcal)				
	Calcite	Aragonite	Chalcedony	Alpha-cristobalite	Fluorite
Meagher County					
White Sulphur Springs-----	-0.68	-0.75	+0.38	+0.11	+0.20
Missoula County					
Lolo Hot Springs-----	-.24	-.31	+.23	-.05	-.95
Park County					
Chico Hot Springs-----	-.23	-.30	+.17	-.10	-1.42
La Duke Hot Springs (A)-----	-.20	-.30	+.09	-.21	+.25
(B)-----	+.12	+.03	+.10	-.19	+.27
Hunters Hot Springs (A)-----	.00	-.09	-.08	-.37	-2.38
(B)-----	-.39	-.48	+.15	-.14	-2.35
Ravalli County					
Medicine Springs-----	-.52	-.59	+.39	+.11	-.27
Sleeping Child Hot Springs (A)-----	-.12	-.19	+.41	+.13	+.14
(B)-----	-.34	-.41	+.48	+.21	+.21
Sanders County					
Camas Hot Springs-----	-.13	-.20	+.09	-.18	-2.17

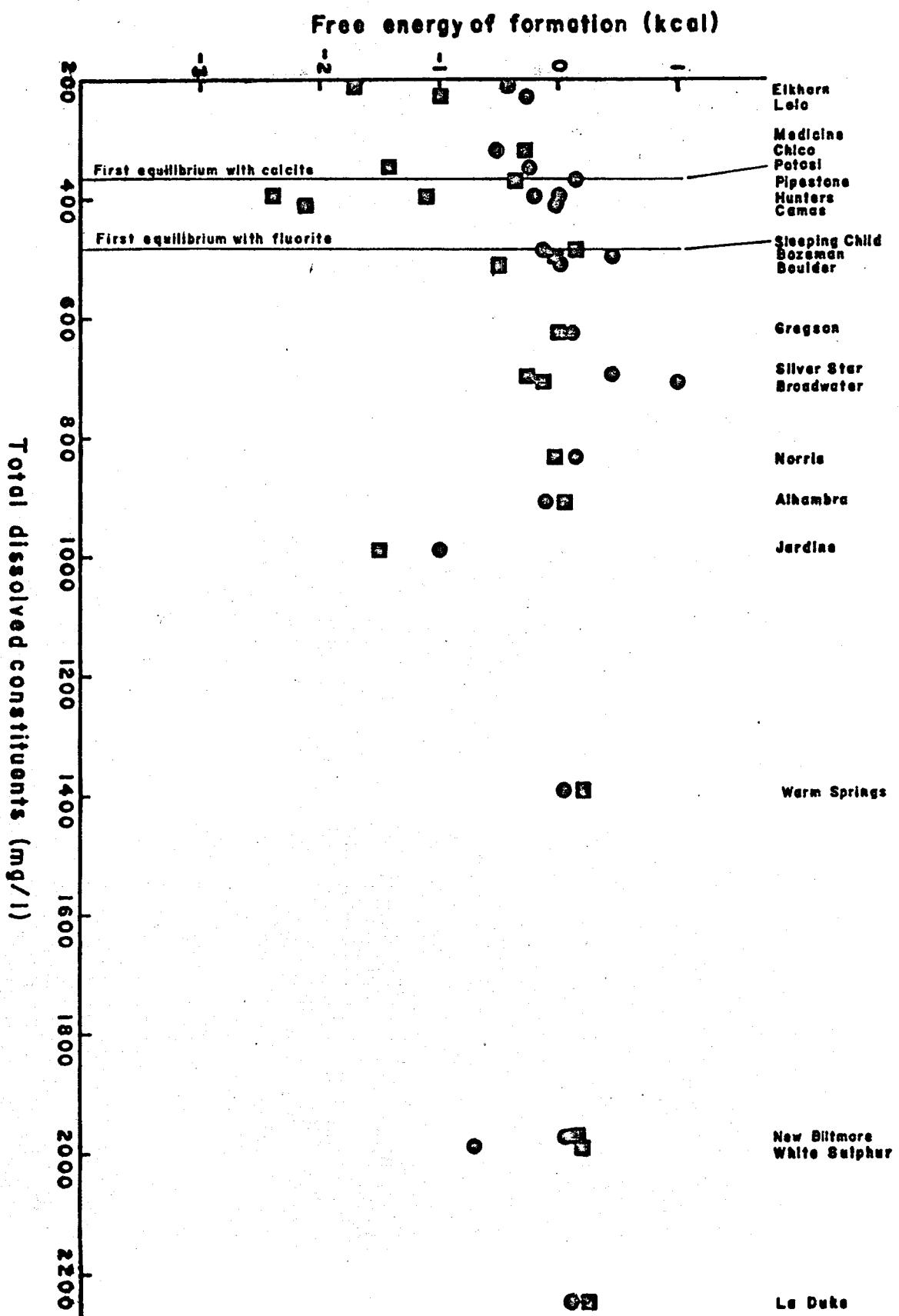


Figure 2. Plot of the calculated free energy of formation for calcite (○) and fluorite (■) as a function of the total dissolved constituents in milligrams per litre.

with a fresh water, absence of calcite and fluorite in the thermal aquifer, or presence of a high temperature system. The proximity of Jardine Hot Springs to a perennial stream and its location on the edge of a sediment-filled basin, makes mixing with a fresh water the more likely explanation. The unsaturation with respect to calcite at White Sulphur Springs is in doubt, due to a pH meter malfunction at the spring. The low total dissolved solids at Boulder Hot Springs makes it difficult to interpret; it may issue a diluted water in which the pH has changed, a conductivity cooled water in which the pH has changed and calcium carbonate has precipitated, or a dilute water in which fluorite was never in equilibrium.

GEOThERMOMETRY

Concentrations of silica and sodium-potassium-calcium in hot springs and shallow hot wells have been shown to indicate semiquantitatively the temperature of the fluid in the associated geothermal reservoir (Fournier and Rowe, 1966; Fournier and Truesdell, 1973). The chemical geothermometers, based on the concentration of silica or the proportions of sodium, potassium, and calcium in the spring waters, are relevant only if the hot spring or well is associated with a hot-water system. These geothermometers are meaningless for the acid sulfate springs associated with dry steam (vapor-dominated) systems such as The Geysers, California, or Larderello, Italy. White, Muffler, and Truesdell (1971) have discussed the salient characteristics of hot water and vapor-dominated systems. All of the hot spring waters discussed in this report have neutral to slightly alkaline pH's and most have flow rates of more than 100 litres per minute, typical of hot water systems. Qualitatively, the low total dissolved solids in the waters and high nitrogen concentration of the hot spring gases indicate that most of the thermal springs in Montana are associated with low temperature reservoirs.

Fournier, White, and Truesdell (1974) have discussed the basic assumptions which must be fulfilled before the quantitative geothermometers can be meaningful. Two of the basic assumptions, that there is negligible re-equilibrium between the water and the country rock as the water flows from the thermal reservoir to the surface and that there has been no mixing of the hot water coming from depth with cool surface waters, are probably violated in some of the sampled waters. Furthermore, they have recommended that springs of large flow rate (more than 100 litres per minute) which issue at less than boiling temperatures be treated as mixed waters if the Na-K-Ca geothermometer indicates a temperature more than 25°C above the temperature of the spring. Also, geothermometers calculated for springs of small flow rate which issue at temperatures below boiling probably give only a qualitative indication of the temperature at depth.

The quartz geothermometer (Fournier and Rowe, 1966) is based on the assumption that the solubility of quartz is controlling the concentration of silica in the hot spring water. However, Arnórsson (1975) has demonstrated that in Iceland the silica concentration of hot springs associated with low temperature reservoirs is controlled by the solubility of chalcedony if the reservoir temperature is less than 110°C and by quartz if the reservoir temperature is more than 180°C; in the intermediate range, 110° to 180°C, either chalcedony or quartz may be controlling the silica concentration. The Na-K-Ca geothermometer could produce erroneous temperature estimates if the water interacted with the country rock after it left the reservoir or if some sodium, potassium, or calcium phases were precipitated as the water moved to the surface. The precipitation of calcium carbonate is probably the most common problem, leading to excessively high reservoir temperature estimates.

The chemical geothermometers, table 8, indicate that at least 13 of the springs are associated with aquifers only slightly hotter than the measured spring temperature. Ten of these low-temperature waters have total dissolved solids of less than 500 mg/l; other low temperature systems have total dissolved constituents of more than 1,300 mg/l. Broadwater Hot Spring is saturated with respect to calcium carbonate, and may be in equilibrium with α -cristobalite at the spring temperature or chalcedony at a slightly higher temperature (96°C). The reservoir temperature at Broadwater is probably near 100°C; however the sampled spring had a very low flow rate. A sample collected by R. B. Leonard during January of this year from an outlet pipe 150 metres downstream from our collection point had virtually the same chemical composition and an acceptable flow rate, 800 litres/minute (R. B. Leonard, written commun., 1976). The Na-K-Ca geothermometers for Jardine and White Sulphur Spring indicate 148°C for both springs. The silica geothermometers may indicate an appreciably lower temperature because of mixing with fresh water. Mixing calculations using the silica mixing model of Fournier and Truesdell (1974) indicate a reservoir temperature near 150°C for both Jardine and White Sulphur Springs if a background silica concentration of 50 mg/l and equilibrium with quartz is assumed. Also, Jardine Hot Spring and probably White Sulphur Springs release some carbon dioxide gas, characteristic of thermal springs associated with higher temperature reservoirs. The sulfate isotope geothermometer, however, indicates a reservoir temperature of 74°C for Jardine Hot Spring (N. Nering, oral commun., 1976). This may indicate that the chalcedony geothermometer is correct (73°C) or it may indicate that sulfide from depth is being oxidized to sulfate in a shallow aquifer where the silica also equilibrates with chalcedony.

Gregson, Alhambra, and Norris hot springs are probably associated with low temperature systems. Two lines of evidence in support of low temperature systems are the minor amount of carbon dioxide in the gas escaping from the springs and the approximate equilibrium with respect to both calcite and fluorite at the spring temperatures. Gregson,

Table 8.--Estimated thermal aquifer temperatures based on the chemical composition of the thermal spring waters

Table 8.--Estimated thermal aquifer temperatures based on the chemical composition of the thermal spring waters--Continued

Spring name	Geothermometers ($^{\circ}\text{C}$) ^{1/}					Comments
	Chalcedony ^{2/}	Quartz	Na-K-1/3Ca	Na-K-4/3Ca	Spring temp. (measured)	
Madison County--Continued						
New Biltmore Hot Springs-----	<u>70</u>	98	178	<u>75</u>	53	Low temperature reservoir.
Meagher County						
White Sulphur Springs-----	70	103	148	127	46	A low temperature reservoir or a mixed water (150°C).
Missoula County						
Lolo Hot Springs-----	<u>60</u>	120	115	<u>76</u>	44	Low temperature reservoir.
Park County						
Chico Hot Springs-----	<u>53</u>	85	183	<u>64</u>	42	Low temperature reservoir.
La Duke Hot Springs (A)-----	<u>71</u>	101	162	<u>75</u>	65	Low temperature reservoir.
(B)-----	<u>70</u>	100	162	<u>76</u>	65	Low temperature reservoir.
Hunters Hot Springs (A)-----	<u>60</u>	114	81	<u>73</u>	60	Low temperature reservoir.
(B)-----	<u>72</u>	114	81	<u>75</u>	57	Low temperature reservoir.
(C)-----	<u>67</u>	114	81	<u>78</u>	60	Low temperature reservoir.
Ravalli County						
Medicine Springs-----	<u>72</u>	110	108	<u>84</u>	45	Low temperature reservoir.
Sleeping Child Hot Springs (A)---	<u>82</u>	115	119	<u>89</u>	52	Low temperature reservoir.
(B)---	<u>80</u>	110	116	<u>82</u>	43	Low temperature reservoir.
Sanders County						
Camas Hot Springs-----	<u>51</u>	118	80	<u>73</u>	45	Low temperature reservoir.

^{1/}Underlined numbers are the geothermometer estimates favored by the authors.^{2/}Dissociation of H_4SiO_4 taken into consideration in calculating the chalcedony geothermometer.

Norris, and Alhambra hot springs are probably associated with reservoirs of 90-115°C. The slight unsaturation with respect to fluorite at Boulder Hot Springs may indicate that some calcium has been lost by calcium carbonate precipitation. Addition of a small amount of calcium in the calculation of the Na-K-Ca geothermometer would improve the agreement between the silica and cation geothermometer. The low PCO_2 calculated for the water from Boulder Hot Springs also favors a low temperature system. Boulder Hot Springs could be associated with a 100°-110°C reservoir in which chalcedony is controlling the silica concentration. Silver Star Hot Springs are probably associated with a thermal aquifer at 110°C. The spring water discharges only minor carbon dioxide and may have lost a small amount of calcium from the water.

ISOTOPES

The isotopic compositions of the 21 hot spring waters are given in table 9. The data are expressed in the δ -notation

$$\delta_x = \left[\frac{R_x - R_{std}}{R_{std}} \right] 10^3 \text{ where } R_x = (D/H)_x \text{ or } (^{18}O/^{16}O)_x$$

of the sample and R_{std} is the corresponding ratio for Standard Mean Ocean Water (SMOW). The areal distribution of deuterium is approximately that expected from the isotopic composition of meteoric waters as reviewed by Taylor (1974). Isotopic compositions of seven fresh waters are listed in table 10. The small oxygen shifts observed in waters from the thermal springs could be a function of the dilute nature of the waters, indicating only minor water-rock interaction, or the age of the system, indicating that the springs are relatively old and the conduits have been flushed of the heavier oxygen isotopes. This second explanation has been given for springs in the Wairakai area of New Zealand where no "oxygen shift" is observed (Craig, 1963; Clayton and Steiner, 1975).

SUMMARY

Fourteen of the twenty-one sampled springs are apparently associated with low-temperature thermal systems ($\leq 100^\circ C$). In these low-temperature systems, Lolo, Sleeping Child, Medicine, New Biltmore, Pipestone, Elkhorn, Potosi, Bozeman, Chico, Warm Springs, Camas, Hunters, Broadwater, and La Duke hot springs, the silica concentration may be controlled by the solubility of chalcedony rather than quartz. Jardine and White

Table 9.--Thermal water isotopic composition in parts per mil (‰)
 [Oxygen and hydrogen isotope ratios are reported relative to Standard Mean Ocean
 Water (SMOW). Oxygen shift refers to the shift in $\delta^{18}\text{O}$ relative to the meteoric
 water line, $\delta\text{D} = 88^{18}\text{O} + 10$.]

Table 9.--Thermal water isotopic composition in parts per mil (‰)--Continued

Table 10.--Isotopic compositions of selected fresh waters in Montana
 [Isotope concentrations are in the per mil notation, relative to SMOW]

Sample	Location	$\delta D (‰)$	$\delta^{18}O (‰)$
Unnamed creek	Near Lolo Hot Springs	-130.9	-17.54
Unnamed creek	Near Sleeping Child Hot Springs	-138.4	-18.05
Unnamed creek	Near Medicine Hot Spring	-141.8	-18.56
Unnamed creek	Near Jardine Hot Springs	-142.5	-18.32
Big Hole River	Near New Biltmore Hot Springs W 1/2 sec. 28, T. 4S., R. 12W.	-140.9	-18.17
South Fork Hot Springs Creek	Near Elkhorn Hot Springs NE 1/4 NE 1/4 sec. 29, T. 4S., R. 12W.	-144.2	-19.03
Unnamed spring	Near Norris Hot Spring NW 1/4 sec. 13, T. 3S., R. 1W.	-150.4	-19.42

Sulphur hot springs have several characteristics typical of mixed waters: they issue at temperatures below boiling, have reservoir-temperature estimates, based on quartz, which are less than the accompanying cation geothermometer, and the cation geothermometer indicates a temperature markedly above the spring temperature. Boulder, Silver Star, Norris, Alhambra, and Gregson hot springs could issue mixed waters or conductively cooled water from low temperature reservoirs. The apparent agreement between the silica (chalcedony) and cation geothermometers along with the nitrogen gas discharging at most of these hot springs leads us to believe that they are associated with low-temperature systems. Even if equilibrium with quartz rather than chalcedony is controlling the silica concentrations, the springs are still associated with low temperature aquifers (110° to 150°C). The apparent equilibrium of the more concentrated waters with fluorite may indicate that only Jardine has been appreciably diluted.

Based on this limited sampling, the hot springs of Montana do not appear to have potential for power generation. Additional work is desirable at Jardine and White Sulphur hot springs, and perhaps Boulder, Silver Star, Norris, Alhambra, and Gregson hot springs.

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