UNITED STATES

DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

CHEMICAL AND ISOTOPIC COMPOSITION OF WATER FROM THERMAL

AND MINERAL SPRINGS OF WASHINGTON

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Open-File Report 82-98

Menlo Park, California

February 1982

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CHEMICAL AND ISOTOPIC COMPOSITION OF WATER FROM THERMAL
AND MINERAL SPRINGS OF WASHINGTON

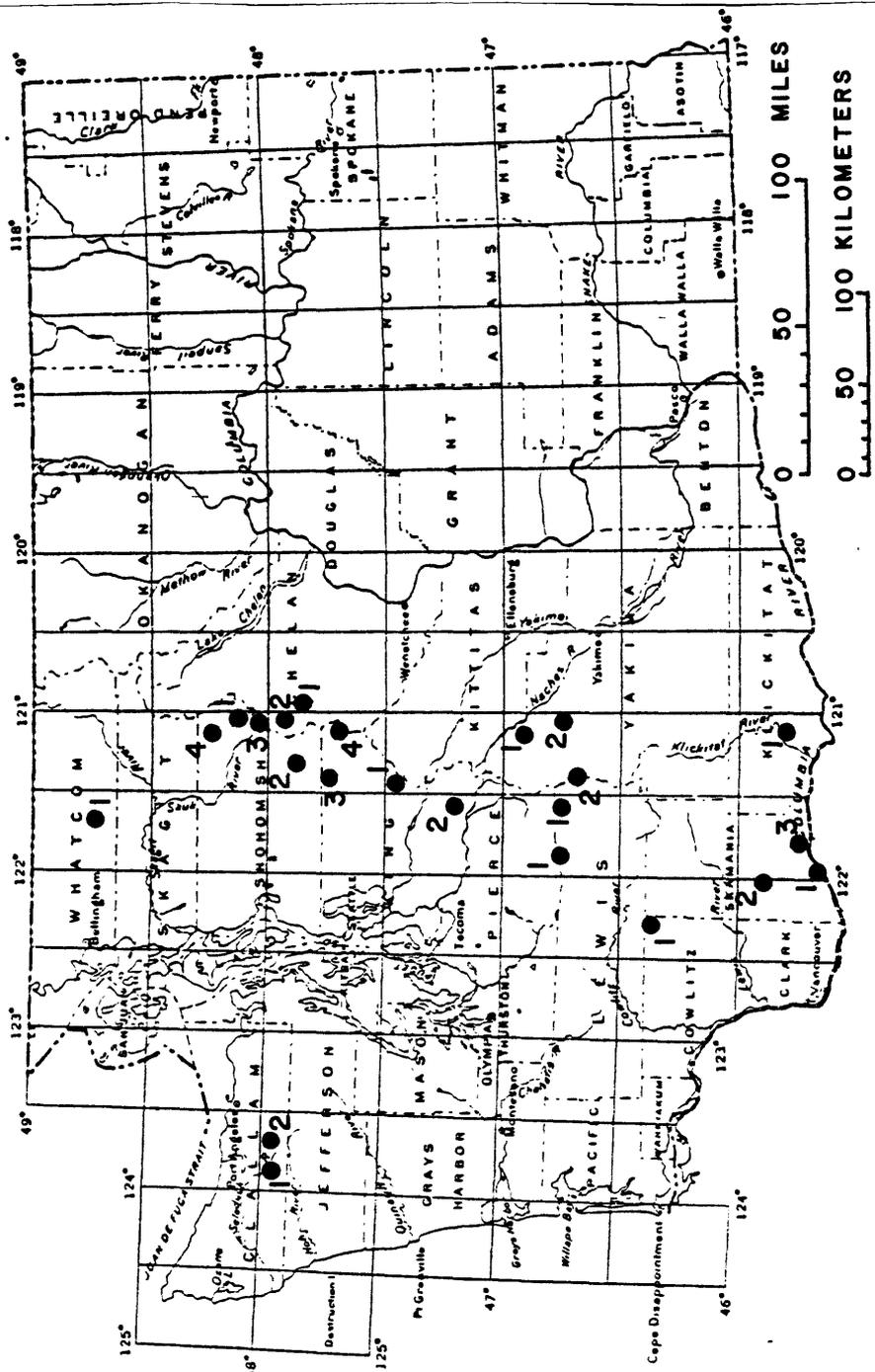By R. H. Mariner, T. S. Presser, and W. C. Evans

ABSTRACT

Waters from the thermal springs of Washington range in chemical compositon from dilute Na-HCO$_3$ to moderately saline CO$_2$-charged Na-HCO$_3$-Cl type waters. St. Martin's Hot Spring which discharges a slightly saline Na-Cl water, is the notable exception. The dilute Na-HCO$_3$ waters are generally associated with granitic intrusions; the warm to hot CO$_2$-charged waters issue on or near the large stratovolcanoes. The dilute waters have oxygen-isotopic compositions that indicate relatively little water-rock exchange. The CO$_2$-charged waters are usually more enriched in oxygen-18 due to more extensive water-rock reaction. The carbon-13 in the CO$_2$-charged thermal waters is more depleted (-10 to -12 °/oo) than in the cold CO$_2$-charged soda springs (-2 to -8 °/oo) which are also scattered throughout the Cascades. The hot and cold CO$_2$-charged waters are supersaturated with respect to CaCO$_3$, but only the hot springs are actively depositing CaCO$_3$. Baker, Gamma, Sulphur, and Ohanapecosh hot springs seem to be associated with thermal aquifers of more than 100°C. As these springs occur as individual springs or in small clusters, the respective aquifers are probably of restricted size.

INTRODUCTION

Berry and others (1980) list 23 thermal springs (greater than 20°C) in Washington. Fumarole fields on Mount Baker, Mount St. Helens, Mount Adams, and Mount Rainier are included in their list along with two warm saline ponds, Hot Lake and Poison Lake in Okanogan County. The saline ponds are density stratified and owe their temperatures to heat from solar radiation trapped in the deeper saline layer. Most of the thermal springs in Washington issue near or just west of the crest of the Cascades (figures 1 and 2). The exceptions are the Warm Springs near Walla Walla, Simcoe Soda Springs, Klickitat Mineral Springs in the Columbia Basin, and Olympic and Sol Duc hot springs in the Olympic Mountains. Packwood, Collins, and Rock Creek hot springs were not sampled because they currently issue in rivers or creeks. Time constraints

WASHINGTON

Chelan County
1. Little Wenatchee River Soda Spr.
2. Little Wenatchee Ford Soda Spr.

Clallam County
1. Olympic Hot Springs
2. Sol Duc Hot Springs

Cowlitz County
1. Green River Soda Spr.

King County
1. Goldmeyer Hot Springs
2. Lester Hot Springs
3. Money Creek Soda Spr.
4. Scenic Hot Springs

Klickitat County
1. Klickitat Springs

Lewis County
1. Ohanapecosh Hot Springs
2. Summit Creek Soda Spr.

Pierce County
1. Longmire Mineral Springs

Skamania County
1. Bonneville Hot Springs
2. Iron Mike
3. St. Martin's Hot Springs

Snohomish County
1. Gamma Hot Springs
2. Garland Mineral Springs
3. Kennedy Hot Springs
4. Sulphur Hot Springs

Whatcom County
1. Baker Hot Spring

Yakima County
1. Bumping River Soda Spr.
2. Goose Egg Soda Spr.

100 MILES

0   50   100 KILOMETERS

Figure 1. Map of the State of Washington showing the location of sampled
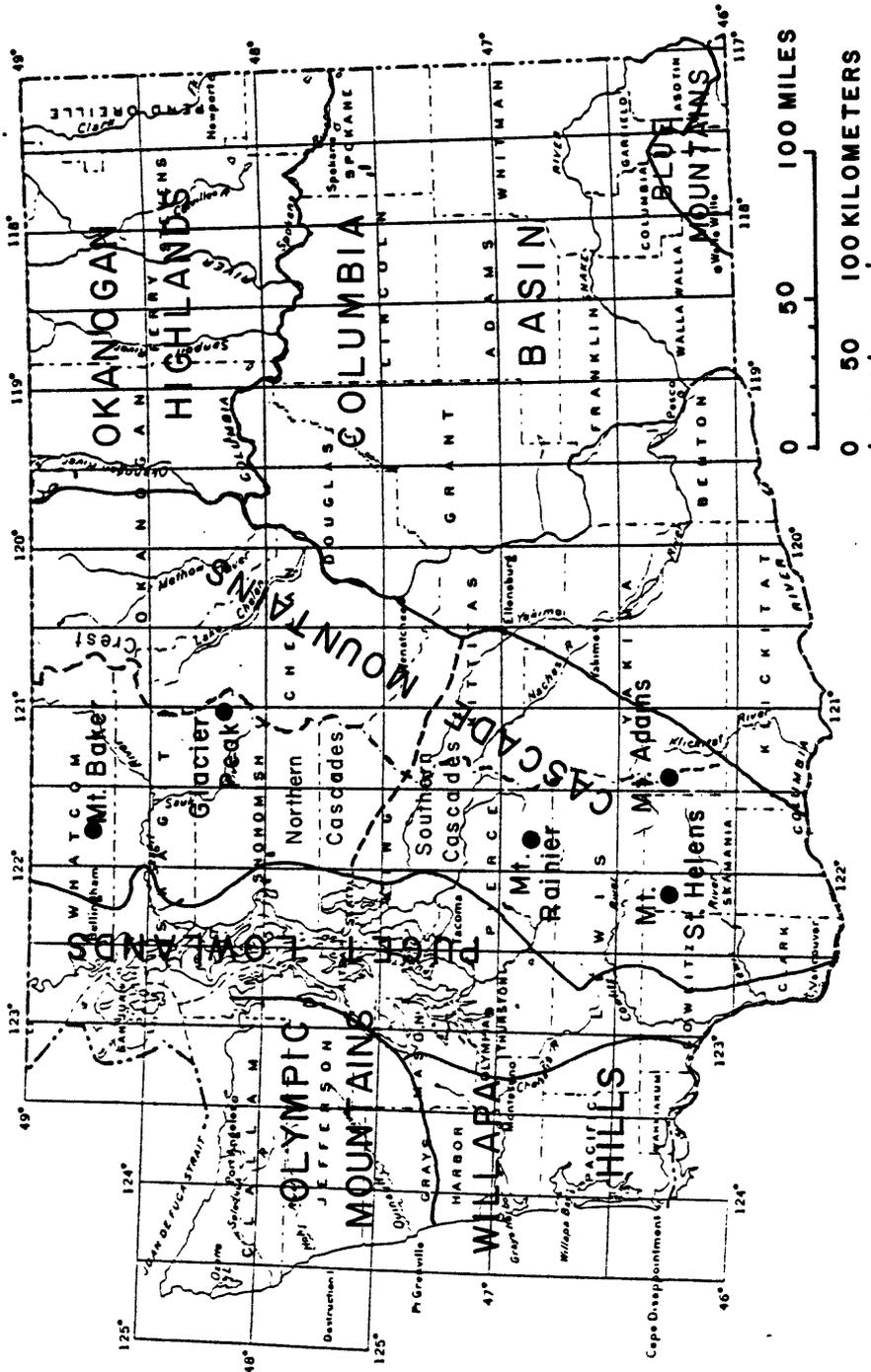thermal and mineral springs.

WASHINGTON

Figure 2. Physiographic divisions of Washington.

did not allow us to sample Klickitat Mineral Springs (27°C), Warm Springs Canyon Warm Springs (22°C), Simcoe Soda Spring (32°C), or Orr Creek Warm Springs (22°C). Cool mineral springs, chiefly soda springs, are also scattered throughtout the Washington Cascades. Green River Soda Spring, west of Mount St. Helens, is reported to have a discharge temperature of 30°C; however, temperatures of 16°C were measured in both April and July 1980. Earlier measurements may have been in error or the spring plumbing may have been changed by seismic activity. Recent chemical analyses for Klickitat Mineral Spring, Government Mineral Spring, and the soda spring on the Green River have been presented by Barnes and others (1981).

The Cascade Range, where most of the thermal and mineral springs occur, can be divided into two geologically different areas (Weissenborn and Cates, 1966). North of Snoqualmie Pass the range consists essentially of a core of granitic rock and metamorphosed sedimentary rocks flanked by younger sedimentary and volcanic rock. South of Snoqualimie Pass, Tertiary volcanic rock with relatively simple structure predominates. Superimposed on the range are the young volcanoes, Mount Adams, Mount Rainier, Mount Baker, Glacier Peak, and Mount St. Helens. The Olympic Mountains consist of a heterogenous metamorphic and plutonic basement complex composed of gneissic amphibolites and quartz diorite overlain by eugeosynclinal sedimentary and volcanic rocks (Wagner and Snavely, 1966). The Columbia Basin, an area of extensive flood basalts of Miocene and Pliocene age, occupies most of southeastern Washington (Griggs,1966).

None of the thermal springs discharge from or are associated with siliceous sinter, an indicator of high subsurface temperature. Ohanapecosh, Kennedy, Garland, and Longmire discharge from travertine mounds. Fossil travertine deposits occur at Gamma Hot Springs within a few feet of the current spring orifices. Gamma Hot Springs discharge in or immediately adjacent to a stream which probably erodes any $CaCO_3$ that is currently deposited by the springs. Of the cold soda springs sampled, only Summit Creek Soda Springs still discharge from a travertine mound, although fossil travertine occurs near several other cold soda springs.

METHODS AND PROCEDURES

The methods of sample collection and field determination of pH, alkalinity, sulfide, ammonia, and aluminum were described by Presser and Barnes (1974). About 2 liters of spring water were pressure filtered through

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a 0.1 micrometer (μm) membrane filter using compressed nitrogen as the pressure source. Filtered water samples were stored in plastic bottles that had been rinsed to remove contaminants prior to use. Samples collected for group I and II metals were acidified to pH 2 or less with concentrated hydrochloric acid. An appropriate amount of deionized water was used to dilute 25 mL of filtered sample to attain dissolved silica concentrations of from 20 to 50 mg/L. Dilutions of 1:2, 1:4, or 1:5 were used. Water temperatures were determined with a thermistor probe or a maximum reading mercury-in-glass thermometer. The pH was determined directly in the spring. Alkalinity was determined immediately after the sample was withdrawn from the spring. Sulfide (total sulfide as H_2S) was precipitated as zinc sulfide from the hot sample. Precipitated samples were stored for as much as 12 hours in a refrigerator before being titrated by the iodometric method. A water sample for ammonia analysis was allowed to cool to air temperature before sodium hydroxide was added to raise the pH to approximately 12. The dissolved ammonia concentration was then measured 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. 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).

Three samples of raw water were collected in 15 mL glass bottles with polyseal caps for stable-isotope analysis. Dissolved carbon dioxide species were precipitated in the field by adding 20 mL of saturated ammoniacal strontium chloride to approximately 100 mL of water from the spring. Samples of any gases escaping from the spring were collected in evacuated gas sample tubes.

Sodium, potassium, calcium, magnesium, lithium, rubidium, cesium, iron, manganese, zinc, and aluminum (field organic extract) concentrations were determined by direct aspiration on a double-beam atomic absorption spectrophotometer. Methods for the analysis of boron, silica, and the anions were described in Skougstad and others (1979). Specifically the methods are: dianthrimide (0.1 to 1.0 mg/L) and carmine (1.0 to 10 mg/L) for boron; molybdate blue for silica; Mohr (>12 mg/L) for chloride; thorin for sulfate; specific ion electrode for fluoride; and hypochlorite oxidation for bromide and iodide. The ASTM (1974) ferric thiocyanide method was used for chloride concentrations <10 mg/L. Mercury was determined by a flameless atomic absorption technique (U.S. Environmental Protection Agency , 1971). These

methods were modified to overcome interferences from iron hydroxide, calcite precipitates, and hydrogen sulfide.

Isotopic ratios of $^{18}O/^{16}O$, D/H and $^{13}C/^{12}C$ were measured on a modified Nier double-collecting 6-inch 60° sector mass spectrometer. The methods of sample preparations were: CO_2-equilibration method of Cohn and Urey (1938) for oxygen; the uranium technique of Bigeleisen and others (1952) for hydrogen; and the phosphoric acid technique of McCrea (1950) for carbonates. Prior to analysis, the $SrCO_3$ precipitate was filtered and washed under an argon atmosphere, dried, and homogenized in a ball mill.

Gases were analyzed by gas chromatography as soon as possible after returning to the laboratory, always within two weeks of collection. Linde Molecular Sieve 5A[1]/ was used to separate and quantify He, H_2, O_2, Ar, N_2, and CH_4, while Porapak Q[1]/ was used for C_2H_6 and CO_2. Helium was used as the carrier gas except in the analysis for He and H_2 where argon carrier was employed.

CHEMICAL COMPOSITIONS

The chemical composition of the thermal and mineral springs are given in tables 1 and 2. The waters may be classified as dilute Na-HCO_3, Na-Cl, Na-HCO_3-Cl, or Na-Ca-HCO_3-Cl type waters. The dilute Na-HCO_3 waters include Olympic, Sol Duc, Goldmeyer, Lester, Scenic, and Bonneville hot springs. The Na-HCO_3-Cl waters are almost all CO_2-charged and include Baker, Gamma, Ohanapecosh, Garland, Kennedy, Goose Egg, Bumping River, Iron Mike, Longmire, Summit Creek, Little Wenatchee Ford, Little Wenatchee River, and Green River. Most of these Na-HCO_3-Cl waters are cool to cold; but Gamma, Ohanapecosh, Kennedy, and Garland have temperatures greater than 20°C. These CO_2-charged Na-HCO_3-Cl waters have pH values of 6 to 6.5 and are slightly to moderately saline. Baker Hot Springs discharge the only dilute alkaline Na-HCO_3-Cl water. St. Martin's Hot Springs discharge the only Na-Cl thermal water in the state. Chemically, the water discharged from St. Martins Hot Springs is similar to the thermal springs that discharge in the Oregon Cascades (Mariner and others, 1980).

Gas discharge rates in the thermal and mineral springs range from slow and sporadic at Olympic, Sol Duc, and Goldmeyer, to rapid and nearly constant at

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1/ The use of brand names is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

Table 1. Chemical composition for the thermal and mineral springs of Washington

[Concentrations are in milligrams per liter]

Name	Water Type	Temperature (°C)	pH	Silica (SiO2)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Lithium (Li)	Alkalinity (as HCO3)	Sulfate (SO4)	Chloride (Cl)	Fluoride (F)	Boron (B)	Hydrogen Sulfide (H2S)
Chelan County															
Soda S. L. Wenatchee R.	CO2-charged	7	6.08	39	320	54	660	39		1715	1	805	0.30	18	<1
Soda S. L. Wenatchee F.	CO2-charged	9	6.48	105	400	73	2120	230		3935	265	2000	.82	45	<1
Clallam County															
Olympic Hot Springs	dilute Na-HCO3	48.5	9.50	66	.9	<.05	72	1.1	.04	175	5	11	1.2	.82	14
Sol Duc Hot Springs	dilute Na-HCO3	51	9.46	60	.8	<.05	80	1.0	.05	181	7	21	1.7	1.4	10
Cowlitz County															
Soda Sp. Green River	CO2-charged	16	6.49	97	225	92	1350	77		2745	<1	1250	.48	27	<1
King County															
Goldmeyer Hot Spring	dilute Na-HCO3	50	8.48	56	6.3	.04	125	3.0		61	40	130	.88	<1	.6
Lester Hot Spring	dilute Na-HCO3	46.5	9.19	61	5.3	.03	105	2.0		61	19	115	1.6	<1	5.7
Scenic Hot Spring	dilute Na-HCO3	47	9.14	44	2.1	.02	49	.64		75	13	22	.72	<1	1.3
Soda Spring Money Creek	CO2 gas discharge no water sample collected														
Klickitat County															
Klickitat Springs	CO2-charged	23	6.11	103	38	38	34	4.3	.05	415	<1	3.7	.84	<.1	<1
Lewis County															
Ohanapecosh Hot Spring	CO2-charged	48	6.80	100	60	4.9	920	52	2.9	1060	170	880	5.2	12	<1
Summit Creek Soda Sp.	CO2-charged	11	6.24	100	240	93	1750	85	5.8	3610	<1	1450	.24	50	<1
Pierce County															
Longmire Mineral Sp.	CO2-charged	19	6.35	125	540	170	580	46	2.2	2700	41	810	.46	3.7	<1
Skamania County															
Bubbling Mike Spring	CO2-charged	15	6.41	75	360	100	585	14	1.0	1610	170	820	.16	21	<1
Iron Mike Well	CO2-charged	18	6.01	65	260	80	420	9.1	.76	1250	120	570	.12	15	<1
St.Martin's Hot Spring	Na-Cl	48	8.54	48	76	.30	360	6.4	.28	19	16	690	.74	2.9	<1
Bonneville Hot Spring	dilute Na-HCO3	36	9.54	46	31	.03	145	.9		39	80	180	.66	2.0	.5
Snohomish County															
Gamma Hot Springs	CO2-charged	65	6.13	141	71	2.8	510	80	2.8	398	30	755	1.4	9.0	2.9
Garland Mineral Spring	CO2-charged	29	6.46	105	390	87	2500	200	9.4	2600	160	3600	1.6	64	<1
Garland Mineral Spring	CO2-charged	24	6.33	95	320	69	2000	150	7.4	2280	130	2700	1.4	48	<1
Kennedy Hot Springs	CO2-charged	35	6.27	175	190	48	670	72	3.5	1660	2	625	1.2	7.5	<1
Sulpiur Hot Springs	dilute Na-HCO3	37	9.35	76	1.2	<.05	100	1.9	.14	154	21	51	3.9	.55	15
Whatcon County															
Baker Hot Springs	Na-HCO3-Cl	44	8.56	103	5.5	.18	170	9.6	.36	165	87	110	3.2	2.7	5.2
Yakima County															
Bumping River Soda Sp.	CO2-charged	9	6.22	95	380	52	290	5.2	.48	1910	<1	190	1.2	2.2	<1
Goose Egg Soda Spring	CO2-charged	10	6.25	92	170	100	260	9.2	.04	1530	2	150	.15	.16	<1

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Table 2. Trace element chemical composition for the springs of Washington

Name	Rubidium (Rb)	Cesium (Cs)	Manganese (Mn)	Iron (Fe)	Ammonium (as N)	Bromide (Br)	Aluminum (Al)	Mercury (Hg)	Zinc (Zn)
	---------- milligrams per liter --------------							----- µg per L ----	
Chelan County									
Soda Springs									
Little Wenatchee R.					0.24		11		
L. Wenatchee Ford					1.7		3		
Clallam County									
Olympic Hot Springs	<0.02	<0.1	<0.01	<0.02	.81			1.1	5
Sol Duc Hot Springs	<.02	<.1	<.01	.04	.72			1.2	5
Cowlitz County									
Soda spr. Green R.					1.5		1		
King County									
Goldmeyer Hot Springs							10		
Lester Hot Springs							10		
Scenic Hot Springs							42		
Klickitat County									
Klickitat Springs	<.02	<.1	.09	4.3				<.1	15
Lewis County									
Ohanapecosh Hot Sprs.	.22	<.1	.07	.04		2.2		<.1	5
Summit Creek Soda Spr.	.32	.1			.45		<1	.1	
Pierce County									
Longmire Mineral Sprs.	.10	<.1	2.6	11		2.8		<.1	30
Skamania County									
Bubbling Mike Springs	.02	<.1	2.6	.06	<1	1.9		<.1	20
Iron Mike Well	<.02	<.1	2.4	13	<1				15
St. Martin's Hot Springs	<.02	<.1	.01	<.02					5
Bonneville Hot Springs							4		
Snohomish County									
Gamma Hot Springs	.52	.15			<.1			.1	
Garland Mineral Sprs.	.47	.2	.92	5.4		7.5		<.1	20
Garland Mineral Sprs.	.36	.15							
Kennedy Hot Springs	.32	.15	.40	3.0		1.8		1.5	350
Sulphur Hot Springs	<.02	<.1	<.01	<.02	.48			.4	5
Whatcom County									
Baker Hot Springs	.04	<.1	<.01	<.02	.45			.4	15
Yakima County									
Bumping River Soda Spr.	<.02	<.1	1.4	15	<.1			<.1	15
Goose Egg Soda Spring	<.02	<.1	1.9	18				<.1	10

Ohanapecosh, Garland, Kennedy, Summit, Green River, Klickitat, Longmire, Bumping River, Goose Egg, Little Wenatchee River, and Little Wenatchee Ford. Springs with constant, rapid discharge rates discharge predominantly CO_2; while springs with slow, sporadic discharge rates, discharge either nitrogen or nitrogen and methane (table 3).

Isotopic data for the thermal and mineral springs are given in table 4. D/H values range from -78.8 to -122.0 $^\circ$/oo and $^{18}O/^{16}O$ values range from -7.37 to -16.53 $^\circ$/oo. D/H values for cold springs immediately adjacent to several of the thermal springs are less depleted isotopicaly, indicating that the thermal springs recharge at higher elevations. Generally, the dilute waters have very small oxygen shifts (<0.4 $^\circ$/oo) whereas the more saline waters have shifts ranging up to +3.7. Carbon-13/carbon-12 values range from -2.6 to -12.6 $^\circ$/oo. In this small set of samples, the hot springs are generally more depleted in carbon-13 than are the cold soda springs.

Many of the cold CO_2-charged springs probably represent old hot-spring systems from which virtually all the heat has been dissipated. Fossil travertine near many of the cold CO_2-charged springs is an indication that the systems discharged hot water in the past. The low temperatures may indicate that all the heat has been discharged from the system or that the water movement is so slowed by minerals precipitated in the channels that all the heat is lost to the surrounding rock before the water discharges at the land surface. Differences observed in C-13/C-12 values between the hot and cold CO_2-charged waters may be produced by different rates of $CaCO_3$ precipitation. Cold CO_2-charged waters retain much more CO_2 and therefore would precipitate less $CaCO_3$ than the hot CO_2-charged waters. Only two $^{18}O/^{16}O$ values are available for dissolved sulfate in the thermal springs: Ohanapecosh (+0.32 $^\circ$/oo) and Garland (+4.71 $^\circ$/oo) (Nehring and others, 1979). The sulfate $^{18}O/^{16}O$ values at Ohanapecosh and Garland hot springs are more depleted than marine sulfate (+10 $^\circ$/oo) but less depleted than values observed in high-temperature geothermal systems such as Lassen (-3 to -4 $^\circ$/oo). Carbon-14 values have been determined only for Longmire Mineral Spring (1.78 $^\circ$/o modern) and Garland Mineral Spring (4.13 $^\circ$/o modern).

GEOTHERMOMETRY

The chemical composition of thermal waters can be used to estimate the last temperature at which chemical equilibrium existed between the thermal water and the country rock. The variables that are most often used include

Table 3. Compositions of gases discharging from srings in Washington
[Compositions are in volume percent]

Name	Oxygen O_2	Argon Ar	Nitrogen N_2	Carbon Dioxide CO_2	Methane [1] CH_4	Helium [2] He	Totals
			Chelan County				
Soda Springs at							
Little Wenatchee River	0.03	0.02	0.79	99.12	0.31	<0.02	100.27
Little Wenatchee Ford	.05	.02	1.22	98.34	<.002	<.02	99.63
			Clallam County				
Olympic Hot Springs[3]	<.02	1.12	53.62	.01	44.84	<.02	99.59
			Cowlitz County				
Soda Spriny Green River	.06	.02	.75	98.83	.10	<.02	99.76
			King County				
Soda Spring Money Creek	.12	.02	1.23	98.68	<.002	<.02	100.05
			Lewis County				
Ohanapecosh Hot Springs	.02	.70	55.09	44.47	.20	<.02	100.48
Summit Creek Soda Spring	<.01	<.01	.05	99.90	.001	<.01	99.96
			Pierce County				
Longmire Mineral Springs	.04	<.02	.09	98.34	<.005	<.02	98.47
			Skamania County				
Bubbling Mike Spring	.17	.02	.98	98.41	<.005	<.02	99.58
Bubbling Mike Spring(1980)	<.02	.02	.76	99.07	<.002	<.02	99.85
St.Martin's Hot Spring	.07	.77	98.47	.01	.30	.08	99.70
			Snohomish County				
Garland Mineral Springs	.10	<.02	.25	99.30	<.005	<.02	99.65
Kennedy Hot Springs	.08	<.02	.36	99.18	.13	<.02	99.75
Sulphur Hot Springs	<.02	1.30	96.67	<.01	.28	.03	98.25
			Whatcom County				
Baker Hot Springs	<.02	1.36	95.54	.09	.70	<.02	97.87
			Yakima County				
Bumping River Soda Spring	.08	<.02	.24	98.55	.02	<.02	98.89
Goose Egg Soda Spring	.14	.02	.44	97.05	<.005	<.02	97.65

[1] C_2H_6 less than 0.05 in all samples.
[2] H_2 less than 0.01 in all samples.
[3] Gas sample from pool at west side of spring group; water sample from a spring on east side of spring group.

Table 4. Isotopic data for the springs of Washington

[Hydrogen and oxygen relative to SMOW; Carbon relative to PDB]

Name	δD	$\delta^{18}O$	oxygen shift	$\delta^{13}C$ CO_2	$\delta^{13}C$ $SrCO_3$	$\delta^{18}O$ SO_4
Chelan County						
Soda Springs						
Little Wenatchee River	-106.5	-13.95	+.61		-9.32	
Little Wenatchee Ford	-107.3	-12.78	+1.88		-6.28	
Clallam County						
Olympic Hot Springs	-95.8	-13.32	+.12			
Sol Duc Hot Springs	-91.8	-12.34	+.39			
Cowlitz County						
Soda Spring Green River	-83.5	-11.39	+.30		-7.72	
King County						
Goldmeyer Hot Spring	-96.2	-13.61	-.34			
Lester Hot Spring	-99.0	-13.41	+.23			
Scenic Hot Spring	-103.4	-14.32	-.13			
Money Creek Soda Spring				-11.76		
Klickitat County						
Klickitat Springs	-111.1	-14.45	+.68		-6.75	
Lewis County						
Ohanapecosh Hot Springs	-120.2	-15.00	+1.28		-11.29	+.32
Summit Creek Soda Spring	-96.6	-11.83	+1.50	-12.23	-9.48	
Pierce County						
Longmire Mineral Springs	-100.4	-12.92	+.86	-13.50	-10.77	
Skamania County						
Bubbling Mike Spring	-79.4	-11.10	+.08	-13.60		
Iron Mike Well	-81.7	-11.09	+.37		-12.64	
Snohomish County						
Gamma Hot Springs	-111.4	-14.29	+.89		-11.08	
Garland Mineral Springs	-78.8	-7.37	+3.73		-7.51	+4.71
Garland Mineral Springs	-80.0	-8.20	+3.05		-7.89	
Kennedy Hot Springs	-105.9	-13.21	+1.28	-11.63	-9.82	
Sulphur Hot Springs	-108.1	-14.52	+.24			
Whatcom County						
Baker Hot Springs	-101.6	-13.89	-.03			
Yakima County						
Bumping River Soda Spring	-122.0	-16.53	-.03	-8.05	-7.10	
Goose Egg Soda Spring	-90.7	-8.93	+3.66	-5.66	-2.59	

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the silica concentration and the proportions of sodium, potassium, calcium, and magnesium. Oxygen-18/oxygen-16 distribution between dissolved sulfate and water has also been used as an indicator of subsurface temperature in geothermal systems (McKenzie and Truesdell, 1977).

Temperatures estimated by geothermetric methods are valid only for hot-water systems and only when certain assumptions are true (Fournier and others, 1974). These assumptions are:

1. Temperature-dependent reactions at depth control the concentration of the consituents used in the geothermometer.

2. The reservoir contains an adequate supply of the reactants on which the geothermometer is based.

3. Water-rock equilibrium is established in the reservoir.

4. The constituents used in the geothermometer do not reequilibrate with the confining rock as the water flows to the surface.

5. Mixing of thermal and nonthermal ground water does not occur.

Ideally, the concentration of dissolved silica in water depends on the temperature of the reservoir and the solubility of quartz. Practically, however, chalcedony rather than quartz limits dissolved-silica concentration in cooler systems, and the temperature at which chalcedony becomes the limiting mineral depends not only on temperature but also on rock type (Arnorsson, 1975). For example, in granitic terrains, quartz limits dissolved silica concentrations to temperatures as low as 70 to 75°C; in basaltic terrains, chalcedony limits dissolved silica concentrations to at least 120°C and possibly 180°C. An additional complication is that the spring pH is higher than 8.5 in many granitic terrains, and at more alkaline pH's, the solubility of quartz or chalcedony is a function of both temperature and pH (Mariner and others, 1980).

Mixing of thermal (high-silica) and nonthermal (low-silica) waters can sharply reduce temperatures estimated from the silica geothermometer. If mixing can be demonstrated, then subsurface temperatures can be calculated using mixing models described by Fournier and Truesdell (1974). Unfortunately, the thermal springs of Washington generally occur as single springs or as small groups of springs that have the same chemical and isotopic composition. Temperature differences are generally minor within a group and are generally a function of flow rate. Mixing is possible in any of the thermal springs, but it has not been demonstrated by chloride-deuterium or chloride-temperature relationships. Mixing models therefore were not used.

The Na-K-Ca and Mg-corrected Na-K-Ca geothermometers are based on empirical relationships between the various cations and measured reservoir temperatures. Temperatures estimated from the cation geothermometers can be sharply increased by loss of calcium after the thermal fluid leaves the geothermal reservoir. Near-surface water-rock reaction with the country rock can release appreciable magnesium and can lead to excessively low temperatures estimated from the Mg-corrected Na-K-Ca geothermometer.

As always, the chemical geothermometers should be used with caution and should be treated as indicators, not measurements. Generally, the Na-Cl or dilute Na-HCO$_3$ waters are less reactive with the confining rock and undergo less change in chemical composition as the water moves from the reservoir to the surface. The CO$_2$-charged waters give the least reliable geothermometry because of their reactive nature, either reacting with the country rock or precipitating CaCO$_3$. Gamma, Baker, and Ohanapecosh hot springs are apparently associated with the highest temperature systems (table 5). Gamma Hot Springs has the highest estimated temperatures (quartz = 157°C, and Na-K-Ca = 216°C); however, at Gamma, dilution is possible and precipitation of CaCO$_3$ is probable. Not only is the water supersaturated with respect to CaCO$_3$, but the dissolved carbon ($^{13}C/^{12}C$) composition is relatively depleted (-11 °/∘∘). Thus the Na-K-Ca may indicate excessively high temperatures whereas the quartz geothermometer may indicate excessively low temperatures. Dilution may also effect Baker Hot Springs. Sulfate-water isotope geothermometer temperatures are not available for either Baker or Gamma Hot Springs. Ohanapecosh Hot Springs appears initially to be associated with an aquifer at a temperature of approximately 140°C on the basis of both quartz and Mg-corrected Na-K-Ca. However, sulfate-water isotope relationships indicate 110°C, as does chalcedony. In addition, the water is supersaturated with CaCO$_3$ and is relatively depleted in carbon-13 (δ $^{13}C/^{12}C$ = -12 °/∘∘). Therefore, it appears that CaCO$_3$ has been lost from the solution as it moved from the reservoir to the surface. The most probable equilibrium temperature at Ohanapecosh is 110°C. Higher temperatures than those indicated from the silica or Na-K-Ca geothermometers are possible in some of the CO$_2$-charged waters. For instance, Garland Mineral Springs (29°C at the surface) has an indicated sulfate-water isotopic equilibrium temperature of 149°C. The high concentration of dissolved silica in the cooler CO$_2$-charged waters probably is a function of the rate of silica mineral dissolution and is not controlled by equilibrium with quartz or chalcedony at elevated

Table 5. Aquifer-temperature estimates for selected springs and wells in Washington

[Temperatures are reported in degrees Celsius(°C)]

Name	Spring	Quartz	Chalcedony	Na-K	Na-K-1/3Ca	Na-K-4/3Ca	Mg-corr. Na-K-Ca
Chelan County							
Soda Springs at							
Little Wenatchee River	7	91	60	141	153	105	81
Little Wenatchee Ford	9	140	114	200	19	89	
Clallam County							
Olympic Hot Springs	48.5	115	86	72	106	91	
Sol Duc Hot Springs	51	111	81	91	100	91	
Cowlitz County							
Soda Spring Green R.	16	136	109	154	15	85	53
King County							
Goldmeyer Hot Spring	50	102	65	92	118	87	
Lester Hot Spring	46.5	100	56	81	108	75	
Scenic Hot Spring	47	65	42	65	90	52	
Klickitat County							
Klickitat Springs	23	139	112	193	159	48	7
Lewis County							
Ohanapecosh Hot Spring	48	137	110	172	171	172	140
Summit Creek Soda Spr.	11	137	110	110	162	161	42
Pierce County							
Longmire Mineral Spr.	19	150	125	159	161	96	46
Skamania County							
Iron Mike Well	18	114	86	87	105	57	53
St.Martin's Hot Spring	48	100	70	78	104	69	89
Bonneville Hot Spring	36	70	31	37	63	24	
Snohomish County							
Gamma Hot Springs	65	157	133	210	216	178	196
Garland Mineral Spring	29	140	114	160	190	196	80
Kennedy Hot Springs	35	171	149	181	189	145	68
Sulphur Hot Springs	37	105	65	81	117	108	
Whatcom County							
Baker Hot Springs	44	139	112	138	162	140	162
Yakima County							
Bumping River Soda Spr.	9	134	107	79	92	32	
Goose Egg Soda Spring	10	133	105	111	121	60	23

temperatures. In the coldest CO_2-charged soda springs, saturation with respect to amorphous silica is approached. Initially, it appears that the quartz geothermometer indicates higher reservoir temperatures than the Na-K-Ca geothermometer in the dilute alkaline waters that discharge at Olympic, Sol Duc, Sulfur, Bonneville, Goldmeyer, Lester, and Scenic hot springs. However, the solubility of quartz or chalcedony in waters as alkaline as these is a function of both temperature and pH. Using one of the solution-mineral computer models such as SOLMNEQ (Kharaka and Mariner, 1977) or ENTHALP (Truesdell and Singers, 1974) it is possible to estimate aquifer pH at sucessively higher temperatures and to determine theoretical equilibrium temperatures between quartz or chalcedony and the respective waters. These estimated temperatures agree more closely with the temperatures estimated from the Na-K-Ca geothermometer. Sulphur Hot Springs discharges the only dilute alkaline water that seems to be associated with an aquifer at temperatures of more than 100°C (110° to 117°C).

DISCUSSION

Although the thermal springs of Washington are associated with an area of young volcanic activity, the chemical data do not indicate the presence of numerous high temperature geothermal systems. Baker Hot Springs and Gamma Hot Springs appear to have the highest temperatures (at least 150°C). Baker Hot Springs appears to be the only system with development potential. The system may have an aquifer temperature of more than 150°C, but it may also be small. Gamma and Ohanapecosh, two of the highest temperature systems, are in wilderness areas or National Parks and are not available for development. Sulphur Hot Springs has an estimated aquifer temperature of only slightly more than 100°C; the low discharge rate, apparently restricted size, isolated location, and moderate temperature, all combine to produce a system of minor importance. All other systems appear to be associated with reservoirs of 115°C or less.

A problem which we have not addressed is the origin of the carbon dioxide in the CO_2-charged waters. Temperatures indicated by the geothermometers for these waters are totally inadequate to explain the generation of the amounts of CO_2 discharged in the springs. The CO_2 is may be generated in the lower crust or upper mantle (Barnes and others, 1978). This CO_2 of deep origin could be dissolved in deeply circulating thermal waters. Variations in the carbon isotopic composition of the dissolved CO_2 in the respective

spring water is probably due to reaction with near-surface limestone; to isotopic equilibration with the limestone if residence times are long enough; or to isotopic depletion if $CaCO_3$ is precipitated from the water as it migrates from depth to the land surface.

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