

Chemical Studies of Selected Trace Elements in Hot-Spring Drainages of Yellowstone National Park

By R. E. STAUFFER, E. A. JENNE, and J. W. BALL

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CHEMICAL STUDIES OF SELECTED TRACE ELEMENTS IN HOT-SPRING DRAINAGES OF YELLOWSTONE NATIONAL PARK

By R. E. STAUFFER,¹ E. A. JENNE, and J. W. BALL

ABSTRACT

Intensive chemical studies were made of S(-II), O₂, Al, Fe, Mn, P, As(III), As(V), and Li in waters from two high-Cl, low Ca-Mg hot-spring drainages in the Lower Geyser Basin, a warm spring system rich in Ca and Mg in the Yellowstone Canyon area, and the Madison River system above Hebgen Lake. Analyses were also made of other representative thermal waters from the Park.

Soluble Al concentrations were generally low (<100 µg/L and frequently <50 µg/L) except in Azure Spring in the River Group of Lower Basin (~500 µg/L). Approximately 90 percent of the Al was found to precipitate in the upper drainage channel and nonflowing satellite pool of Azure Spring and was accompanied by an 8 percent (250 µg/L) loss of the Li flux.

Solute Fe and Mn concentrations were typically very low (<10 µg/L) in the alkaline high-Cl thermal waters. Soluble reactive P and total P concentrations were low (<2 µg/L as P) in all of the high-Cl, HCO₃-buffered hot springs. The Firehole, Gibbon, and Madison Rivers contained 4 to 6 µg/L.

Total solute As acted conservatively in the alkaline drainages studied, including the Firehole-Madison River. However, the As(III)/As(V) ratio was strongly bimodally distributed (~50 or <0.1) according to whether dissolved S(-II) or O₂ was dominant in the thermal water. Oxidation of As(III) proceeded rapidly at the elevated temperatures (30° to 90°C) in the drainages, but only following the oxidation of dissolved S(-II). In contrast to the Firehole River, approximately 60 percent of the thermally related As flux in the Gibbon River drainage basin is precipitated prior to the Gibbon's confluence with the Firehole at Madison Junction. The As/P atomic ratio is typically ~500 for the alkaline hot-spring waters, and ~15 during base-flow conditions on the Madison River. The differential toxicities of the As species, the variable As(III)/As(V) ratios, and the very large As/P ratios all suggest that As may be ecologically important in the Park's thermal waters.

INTRODUCTION

The trace-element chemistry of hot springs and geothermal drill-hole waters has attracted interest in the past because of the hypothesized relationships between hydrothermal solutions and base metal ore genesis (Barnes, 1967). Trace-element chemistry is also valuable in assessing both subsurface physical-chemical conditions and potential environmental impacts of geothermal commercial exploitation.

The principal solutes present in hot-water-

dominated geothermal fluids, SiO₂, Na, K, Li, Ca, Mg, Cl, HCO₃, SO₄, F, and B, have been investigated in diverse geothermal settings throughout the world (Ellis, 1970). The concentrations of the prominent nonconservative solute species (SiO₂, Ca, Mg, F, K) have been rationalized using mineral equilibria models (Ellis, 1967, 1970, 1973). The rare alkalis, Cs and Li, and the metalloid, As, are regarded by Ellis (1970) as weakly conservative because they are sometimes partially precipitated in the epithermal zone. The elements Cl, Br, and B are considered highly conservative, once dissolved in the hot circulating water.

Ellis (1969, 1973) interprets the low levels of Fe, Mn and Al in HCO₃-buffered hot waters as convincing evidence that solubility controls are acting on these geochemically abundant elements. Sulfides of Fe, Cu, Pb, and Zn are being deposited at depths of 250 to 800 m at both Waiotapu and Broadlands, New Zealand (Browne, 1969), from hot water containing up to 1.7, 10, and 2.2 µg/L (micrograms per liter) of the latter three elements, respectively (Ritchie, 1973). Heavy-metal mineralization at depth is largely absent at Wairakei, although some pyrrhotite (FeS) is found. The abundant mineralization at Broadlands is attributed to the high concentration (120 mg/L) of solute sulfide species, S(-II), in the effluent. At Wairakei, S(-II) is 12 mg/L, or about one order of magnitude larger than most of the values reported for Yellowstone (Thompson and others, 1975) or Steamboat Springs, Nevada (White, 1967). Spectrographic analyses of evaporated residues of typical alkaline Yellowstone thermal waters (Rowe and others, 1973) indicate levels of transition series elements comparable to New Zealand thermal waters (Ellis, 1969).

Greater than milligram-per-liter concentrations of Fe, Mn and Al commonly occur in "acid-sulfate-type" geothermal waters as a result of attack on the country

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rock by sulfuric acid (White and others, 1971). The sulfuric acid is thought to be derived from oxidation of S(-II) in the near-surface zone.

White (1967) noted that the semimetallic elements As, Sb and Hg are especially mobile in geothermal systems and are present at relatively high concentrations. Sb and Hg sulfides are epithermally deposited along with sinter at Steamboat Springs (White, 1967) and at Broadlands (Weissberg, 1969). Neither of the two prominent arsenic sulfides (orpiment, As_2S_3 ; realgar, AsS) was observed as a discrete mineral, either in the sinter or at depth in drill cuttings. However, As coprecipitated with stibnite (Sb_2S_3) as ~5 percent impurity (Weissberg, 1969). Weissberg noted that Tl, Ag, Au, and Hg, in addition to As, were highly enriched in stibnite in the near surface at the Broadlands. Arsenopyrite in minor amounts has been ejected from a Wairakei drillhole. Weissberg (1969) estimated that less than 10^{-4} percent of the As flux from a Broadlands drill-hole discharge was precipitated with the amorphous silica, in contrast to 0.5 to 5 percent of the Sb.

Research on the thermally related fluxes of Hg and As into the Waikato River (Axtmann, 1975) was motivated by geothermal power development in the Taupo Basin, New Zealand. Elevated levels of both As and Hg were found in the sediments of Lake Aratiatia below the discharge of the Wairakei effluents. The macrophytic dominant in Lake Aratiatia, *Lagarosiphon* major, featured an As concentration factor (over the Waikato River concentration of $39 \mu\text{g/L}$) of 5,300 (Reay, 1973). However, because of the very large As flux in the Waikato (estimated at 158 metric tons/yr, Axtmann, 1974), less than 4 percent of the As entering the river system is removed by vegetation before discharge into the sea.

The attenuation of geothermally related trace elements in hot-spring drainages and receiving waters has apparently not been previously studied in the United States. Boylen and Brock (1973) and Zeikus and Brock (1972) reported chemical analyses of the Firehole River (Yellowstone Park, Wyo.) at stations selected to show qualitative influences of hot-spring influents on the river biota. Among the elements which can properly be thought of as geothermal trace elements, only PO_4 data were reported and were seriously biased by an As interference (Stauffer, 1980a, b).

The present paper reports chemical studies of O_2 , S(-II), Al, Fe, Mn, As, P, and Li in two hot-spring drainages in the Lower Geyser Basin, two warm-spring drainages in the Yellowstone Canyon, and the Madison River system above Hebgen Dam. The differential effects on the solutes of temperature, pH, and redox changes accompanying adiabatic cooling and source water mixing are examined using the conservation of

mass principle and employing statistical contrast with Cl as the prominent conservative geothermal tracer. Our use of ratio estimation involving Cl as a tracer follows the early initiatives of Ellis and Wilson (1960). The intensively studied thermal drainageways are also compared chemically with representative springs sampled in the Upper, Norris, and Mammoth thermal basins.

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SAMPLE SOURCES

LOWER GEYSER BASIN

The most intensive geochemical studies on hot-spring drainages were on Octopus Spring (Marler, 1973, p. 435), in the lower White Creek area, and Azure Spring (Marler, 1973, p. 574), in the River Group (Fig. 1).

Octopus Spring, with its long (~50 m) distinct drainage channel, relatively constant flow regime, easy accessibility, and luxuriant microbiological flora, is one of several sites in the lower White Creek area where the ecology of thermophilic blue-green algae and associated bacteria has been intensively studied by T. D. Brock and coworkers (Brock, 1967, 1969; Brock and Brock, 1966, 1967, 1968a, b, 1969a, b; Walter and others, 1972).

Azure Spring has a well-developed drainage channel ~100 m in length discharging westward into the Firehole River. The hotter satellite pool on the southwest edge of Azure Spring's main pool was also sampled. Azure is one of a large number of springs in the River Group on which major chemical constituents have been determined (Thompson and others, 1975).

Sampling stations along the two drainageways were selected to correspond to ~10°C intervals in water temperature.

YELLOWSTONE CANYON

An unnamed sulfide-bearing spring was studied, which is 20 to 30 m vertically above the west bank of

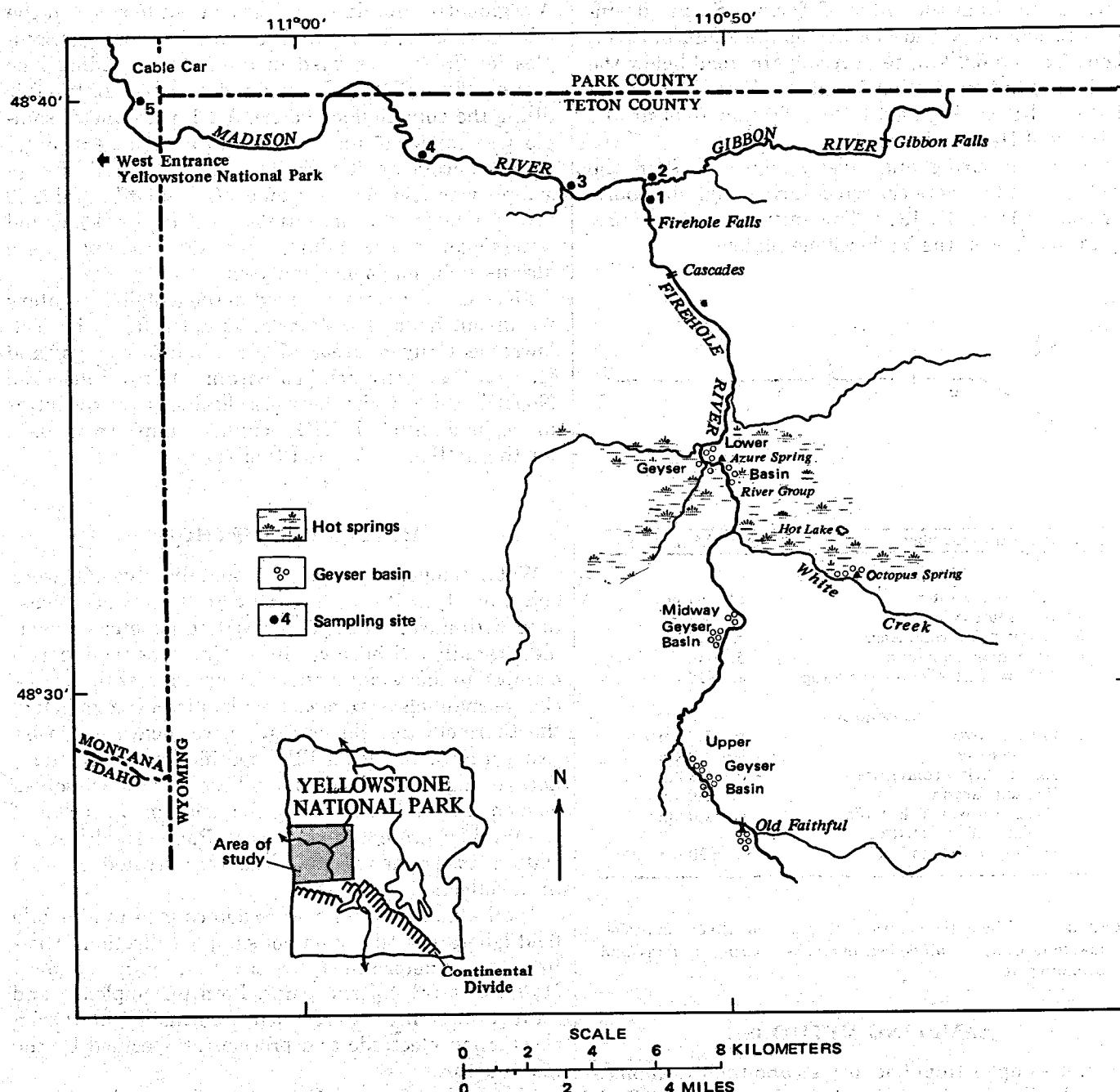


FIGURE 1.—Sketch map showing rivers and major hydrothermal areas sampled in Yellowstone National Park, Wyo.

the Yellowstone River, about 0.5 km south of Tower Falls. About 5 m below its source in a hillside fissure, the spring water (46°C) mixes with water from a cooler (14°C) spring (fig. 2). Below the confluence the mixed water runs steeply downslope until it encounters a relatively flat, poorly drained area, 5 to 10 m above the Yellowstone River. Samples were taken in both tributary spring drainages about 1 m above the confluence, immediately below the confluence, at the bottom of a

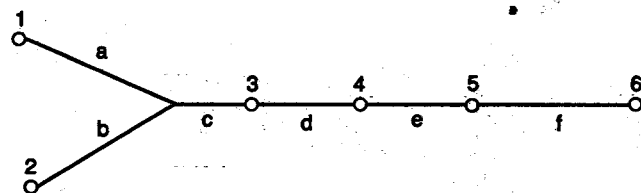
small riffle, at the base of the steeply dropping combined drainage section, and at a point intermediate between the confluence and the base. Below station 5 the drainage into the Yellowstone River was indistinct.

MADISON RIVER SYSTEM

Stations 1 and 2 are on the Firehole and Gibbon Rivers, respectively, each about 1 km above their confluence forming the Madison River. Station 2 is

downstream from the entry of Terrace Spring drainage. Stations 3 and 4 are located on the Madison River, about 1.8 and 6.0 km, respectively, by road below the confluence (fig. 2). Station 5 is at the West Yellowstone Madison River Gaging Station. Station 6 is at the spillway of Hebgen Dam.

All of the spring and river samples used in the drainage studies were collected during daylight hours, September 18 to 27, 1974. The entire period was precipitation free on the Yellowstone plateau.



Sampling sites (numbers)	Distances (horizontal)
Yellowstone Canyon	
1. 40°C source water	a. ~1 m
2. 14°C source water	b. ~1 m
3. Station below confluence	c. ~0.5 m
4. Down drainage station	d. ~10 m
5. At base of steeply sloping drainage	e. ~15 m
Madison River	
1. Firehole River	a. 1.0 km
2. Gibbon River	b. 1.0 km
3. Madison below confluence	c. 1.8 km
4. Madison Canyon	d. 6.0 km
5. Madison at West Yellowstone gaging station (inactive)	e. 12.0 km
6. Spillway of Hebgen Lake	f. ~30 km

FIGURE 2.—Schematic diagram of Madison River and Yellowstone Canyon sulfide-bearing mixed spring systems and sampling sites.

SAMPLING METHODS

Water samples from hot springs and their drainages were obtained and processed as described by Ball, Jenne, and Burchard (1976). Briefly, the samples were obtained with a Masterflex² portable electric pump equipped with silicone tubing. Filtered samples were obtained by attaching a barrel-less pressure filter assembly (142 mm diameter, 0.1 μ m pore size) to the silicone outflow tube of the pump (Kennedy and others, 1976). This arrangement allowed sample collection from boiling hot springs without air contacting the sample, and with a maximum temperature drop of 2°C.

²Mention of brand names is for the convenience of the reader and does not constitute endorsement by the U.S. Geological Survey.

A segmented aluminum pole was used to suspend the inlet tube over, and into, the large hot springs. Samples for S(-II) were fixed in the field by adding zinc acetate (50 mg/250 mL of sample) immediately after filling the polyethylene bottle. A 1 L trace-metal sample was collected and acidified to a pH of 1.0 to 1.3 using concentrated redistilled HNO₃. Another subsample was acidified with concentrated HCl (1 mL/250 mL sample) for determination of As (III), As (V), P, and some major cations. Filtered-unacidified samples were also used for major ion analyses.

Most samples were acidified in the mobile laboratory within an hour of collection; samples from the Yellowstone Canyon area, Mammoth hot springs, and Hebgen Dam were acidified within 10 hr of collection. No HCl-acidified samples were obtained from the latter areas; hence filtered HNO₃-acidified samples were used for the As(III), As(V), and P analyses.

ANALYTICAL METHODS

Water temperature, pH, Eh, and dissolved O₂ were determined onsite. Spring temperatures were measured with a calibrated mercury thermometer on samples rapidly withdrawn in a Thermos-type bottle clamped to the sampling pole. Temperatures in the discharge channels were measured by direct immersion of the thermometer. Eh and pH were measured onsite using a Sargent Model PBX specific ion meter and a flow-through cell (Ball and others, 1976). Dissolved oxygen was measured using the azide modification of the Winkler procedure (American Public Health Association, 1971); the fixed samples were titrated within 3 hr of collection.

Total alkalinity and F were determined in a mobile field laboratory on the day of sample collection. Alkalinity was determined by titration with standard H₂SO₄ to a pH 4.5 end point. Both uncomplexed and total F activities were measured using an Orion specific ion electrode and procedures specified by the manufacturer.

Li, Na, K, Mg, and Ca were determined by flame atomic absorption using a Perkin Elmer Model 303 or 306 spectrophotometer, following procedures issued by the manufacturer. SiO₂ was analyzed by direct current plasma spectroscopy using a Spectrospan III operating in single element mode.

Cl and SO₄ were determined by cation exchange using a refinement (Stauffer, 1980b) of the method of Mackereth (1963). The refinement was necessary to cope with the high F levels in Yellowstone Park thermal waters. P, As(III), and As(V) were determined following an adaptation (Stauffer, 1980b) of the molybdate procedure of Johnson and Pilson (1972a).

Fe, Mn, and Al were determined using flame atomic absorption spectrometry, following 8-quinolinol MIBK extractions. Al was also extracted from filtered, unacidified, cooled water samples on the day of sampling following the procedure of Kennedy, Zellweger, and Jones (1974). Field-extracted Al (back extracted from MIBK into 1.0 molar HNO₃) was subsequently analyzed by flame atomic absorption.

Total dissolved Sb was analyzed using a modification (Stauffer, 1977) of the Yanagisawa, Takeuchi, and Suzuki (1973) atomic absorption procedure.

Total dissolved S(-II) was determined on fixed samples using the potentiometric procedure of Baumann (1974).

RESULTS

DATA RELIABILITY

PURE ANALYTICAL ERROR

Identification of chemical processes acting in the hot-spring drainages depends in part on the magnitude of the analytical errors. Estimates of the analytical coefficients of variation (c.v.) for pertinent solute levels and the most important solute species are contained in table 1. The errors (table 1) apply to individual variates; the variance of the mean \bar{X} of n independent identically distributed (statistically) X values is given by equation 1 (Hogg and Craig, 1970):

$$\text{Var } \bar{X} = \text{Var } X/n. \quad (1)$$

The mean square errors (squared bias plus variance) for K and Li are the smallest. The low levels of Ca and particularly Mg in the "typical" alkaline Upper or Lower Basin hot springs imply large analytical coefficients of variation.

In general, the low levels of SO₄ and high concentrations of F in the Upper and Lower Basins result (table 2) in significant potential biases in SO₄ estimates obtained using the cation-exchange method. The problem is ameliorated considerably in the river waters, and in hot-spring waters from north of Madison Junction, because of large associated increases in the SO₄/F molar ratio (Rowe and others, 1973; Thompson and others, 1975). Because of the dominance of Cl in most of the waters being considered here, the Cl data has a c.v. of 1 percent, about equal to that for data published elsewhere on these waters (Rowe and others, 1973; Thompson and others, 1975).

Errors associated with the As and P species are discussed in detail elsewhere (Stauffer, 1980a, b). The P levels in the typical alkaline hot-spring waters are

TABLE 1.—Analytical precision of solute data

Solute	Analytical method*	Level (mg/L)	Coefficient of variation** (c.v.) (percent)	Remarks
Li	Flame AA	0.50	0.3-0.5	C.v. insensitive to level.
Li	do.	5.00	3-5	
Na	Flame AA	100	5	C.v. becomes progressively worse for levels under 100 mg/L
Na	330 nm line	500	2-3	Probably most sensitive method.
K	Flame AA	10.0	2-3	
Mg	do.	.1	3.6	
Mg	do.	1.0	2.0	
Ca	do.	1.0	2.5	Sensitive to SO ₄ and NO ₃ interferences.
Ca	do.	5.0	1.0	C.v. increases approximately as the term [1 + (SO ₄ + F)/Cl] when F, SO ₄ , and Cl are expressed in milliequivalents.
Cl	Conductivity, cation exchange.	50	1.0	C.v. increases with non-zero F, SiO ₂ levels.
SO ₄	do.		1.0	
F	Specific ion electrode.	30	2.0	
Alkalinity	Titration	200	1.0	Noncarbonate alkalinity may be >25 percent of total.
As	Spectrophotometric Mo-blue.	.20	2.0	C.v. increases with decreasing level, sensitive to PO ₄ at low level.
As	do.	2.00	.3	
Al	Flame AA, solvent extracted in field.	.10	8.3	
Al	do.	.025	12.0	
Al	extracted in lab	.200	7.0	
Sb	Flame AA, lab solvent extracted.	.25	4.0	Recovery dependent upon volume solvent extracted.
Sb	do.	.5	2.0	
Mn	Flame AA, lab solvent extracted.	.001	5	
Mn	do.	.010	2	
Fe	Flame AA, lab solvent extracted.	.003	1.5	
Fe	do.	.020	2.5	
O ₂ (aq)	Winkler	1.0	5.0	
S ⁻²	Specific ion electrode.	8.0	1.0	
S ⁻²	do.	3.0	3.0	

*AA = Atomic absorption.

**Coefficient of variation (c.v.) = $100 s_x/\bar{x}$ when s_x is the estimated standard pure analytical error for an individual replicate.

near the detection limit of $\sim 2 \mu\text{g/L}$. At these low levels the P estimates are also positively biased by the very large concentrations of SiO₂ invariably present in geothermal waters. The relative root-mean-square errors and c.v. for total As are among the smallest for any of the solutes analyzed in these hot-spring waters. Both the accuracy and precision of the total As components, As(III) and As(V), suffer, however, from uncertainties in the preservation of As(III) at the time of sampling of the boiling hot-spring waters, as well as methodological constraints associated with molybdenum-blue (Stauffer, 1980a, b).

The precision of the total F data decreases at the low concentrations found in high-Ca waters in Yellowstone Canyon.

The c.v. for S(-II) is likely to be small compared with ZnS oxidation biases which may have resulted from 3 months of storage of the samples prior to analysis. Possible oxidation effects (resulting in negative biases) were not evaluated. However, Brock, Brock, Bott, and Edwards (1971), citing thesis work of Pachmayr, state that the ZnS precipitates are stable against oxidation for weeks. The sulfide data reported here are likely to be minimum values.

TABLE 2.—Chemical and physical parameters of Octopus Spring and its drainage
 (Temperature, Eh, pH, and O₂ are field determinations; other analyses performed after return to Menlo Park Laboratory, except as noted)

Parameters ¹	Station No. of spring and its drainage							Concentration	
	1*	2	3	4	5	6	7*	Difference ² (7-1)	Ratio ³ (7/1)
Sample 74WA	112	114	115	116	117	118	113	---	---
Temperature (°C) ⁴	82-85	63-75	53-61	50	40	30	23-26	-59	n.a.
pH	7.78	---	8.3	8.6	8.8	9.0	8.65	+87	n.a.
Eh (mV)	+18	+242	+288	+305	+289	---	+332	+314	n.a.
O ₂ (aq) (mg/L)	.92	2.68	3.93	5.38	5.90	6.65	6.78	+5.9	n.a.
Alkalinity (mg/L)	340	---	---	---	---	---	367	+27	1.08
Na (mg/L)	307	317	322	326	336	335	332	+25	1.08
K (mg/L)	15.2	15.4	15.5	16.1	16.5	16.4	16.4	+1.25	1.08
Li (mg/L)	3.42	3.53	3.57	3.64	3.72	3.75	3.72	+30	1.09
Mg (mg/L)	.009	.018	.007	.008	.010	.009	.010	---	---
Ca (mg/L)	.54	1.27	.64	.64	.79	.59	.73	+19	1.35
SO ₄ (mg/L)	21	---	---	---	---	---	23.0	+2	1.14
Cl (mg/L)	262	269	269	262	275	286	284	+22	1.08
F (mg/L)	22.0	---	---	---	---	---	25.0	+3.0	1.14
SiO ₂ (mg/L)	270	256	257	258	261	216	219	-51	.815
S ²⁻ (μg/L)	<15	---	---	---	---	---	<15	---	n.a.
Al (FI) (μg/L)	41	---	---	---	---	---	47	+6	n.a.
Al (FI) (μg/L)	47	---	---	---	---	---	16	-31	n.a.
Al (UI) (μg/L)	51	54	64	26	9	33	47	-4	n.a.
Fe (FI) (μg/L)	2.8	---	---	---	---	---	3	+2	n.a.
Fe (UI) (μg/L)	1.4	---	---	---	---	---	---	---	n.a.
Mn (FI) (μg/L)	3.0	---	---	---	---	---	.7	-2.3	n.a.
Mn (UI) (μg/L)	3.4	3.7	3.4	3.1	5.0	1.1	.8	-2.6	n.a.
As (V) (μg/L)	1,380	---	---	---	---	---	1,610	+230	n.a.
As (V) + As (III) (μg/L)	1,455	1,525	1,510	1,545	1,575	1,630	1,620	+160	1.11
Sb (μg/L)	58	---	---	---	---	---	---	n.a.	n.a.
P* (μg/L)	2	---	---	---	---	---	.9	-1.1	n.a.

*Filtered samples, except as noted. Stations 2-6 were unfiltered.

¹FI = filtered and field extracted; FI = filtered and lab extracted; UI = unfiltered and lab extracted.

²Concentration at station 7 minus that at station 1.

³Concentration ratio of station 7 to station 1.

⁴Temperature variations in response to discharge periodicity was measured at selected stations only.

⁵Not applicable.

⁶Soluble reactive phosphorus as P (Strickland and Parsons, 1968).

The alkalinity data were adjusted for partial protonation of F (Ellis, 1963) and incomplete protonation of HCO₃ at the pH = 4.5 alkalinity end point. Corrections for the protonation of dissolved borates and silicates were not made. However, the protonation of dissolved silicates may introduce an error in some instances (D. V. Vivit and others, unpub. data, 1978).

Among the solvent-extracted elements quantified by atomic absorption (Al, Mn, Fe, and Sb), Al and Sb suffer from the largest analytical variances. Low levels of Al tax the sensitivity constraints on Al analysis by flame; flameless atomic absorption for Al is inherently imprecise. Furthermore, the field extractions of Al have error components resulting from the following factors: (1) Field constraints prevented extracting the samples immediately after sampling; in fact, the time lag varied from 1 to 24 hr; (2) the solution temperature during the extraction procedure varied from about 6° to 50°C, with possible effects on solvent-extraction efficiency. The Sb procedure is influenced by SiO₂ levels; the high and variable levels of SiO₂ in the hot-spring waters and the very complex polymerization chemistry of SiO₂ contribute the major analytical component of variance to the Sb analyses (Stauffer, 1977).

SAMPLING ERRORS

Although physical-chemical conditions in the springs are relatively invariant, the estimated concen-

trations of solutes at fixed points along the down drainages vary (time scale = minutes) with spring discharge. The channel-water temperatures are positively correlated with discharge, and evaporative cooling results in a concentration of solutes in the remaining liquid phase. From the Bowen equation (Bowen, 1926) it can be shown that 95 percent of the heat dissipation of 85°C (spring orifice temperatures) and 88 percent of the heat dissipation at 50°C is evaporative (latent heat transfer). A latent heat transfer model implies a 0.18 to 0.19 percent increase in conservative solute concentration for each 1°C of evaporative cooling. The sun's radiant heat input may approximate 15 cal/g water. A purely latent heat transfer model approximates total water losses through evaporation in the channel. Thus, the small amount of sensible heat exchange is approximately balanced by dissipation of the added radiant energy.

Drainage stations could not be synoptically sampled; thus variable spring discharge introduces a within-station and a between-station component of sampling variance to the estimated solute concentrations. Based on the coefficient 0.19, and the observed short-term temperature variations in the Lower Basin drainages studied (tables 2, 3), the "sampling" component (c.v.) of solute concentration errors is ~1.0 percent, a value larger than the analytical "pure error" for the major alkali ions but ≤ analytical c.v.'s for the major anions (table 1). The analytical and sampling errors should be

TABLE 3.—Chemical and physical parameters of Azure Spring and its drainage
 [Temperature, Eh, pH, and O₂ are field determinations; other analyses performed after return to Menlo Park laboratory, except as noted.]

Parameter ¹	Station No. of spring and its drainage						Concentration		
	1*	1*	2	3*	4	5*	Difference ² (5-1)	Ratio ³ 5/1	1/1 ⁴
Sample 74WA	136	132	135	133	137	134	---	---	---
Temperature (°C) ⁵	89	86	64-70	45-63	49-50	33-41	-49	1.09	n.a.
pH	7.49	8.62	9.18	9.25	9.20	9.42	+80	n.a.	n.a.
Eh (mv)	-76	-185	-36	+75	+351	-342	+527	n.a.	n.a.
O ₂ (aq) (mg/L)	.0	.0	.38	1.78	2.62	4.78	+4.78	n.a.	n.a.
Alkalinity (mg/L)	311	322	328	332	337	353	+41	1.06	1.04
Na (mg/L)	13.4	13.8	14.5	15.0	14.6	14.6	+80	1.06	1.03
K (mg/L)	2.93	3.23	3.10	3.16	3.16	3.30	+0.7	1.02	1.10
Li (mg/L)	.079	.028	.054	.018	.027	.075	+0.05	2.68	.354
Mg (mg/L)	2.10	1.20	1.14	1.21	1.49	1.25	+0.05	1.04	.571
Ca (mg/L)	50	52	---	49	---	55	+3	1.06	1.0
SO ₄ (mg/L)	310	316	---	342	321	352	+36	1.114	1.02
Cl (mg/L)	28.6	29.8	---	31.0	---	32.5	+2.7	1.091	1.04
F (mg/L)	---	240	230	226	230	210	-50	.875	---
SiO ₂ (mg/L)	---	1,500	---	60	---	20	-1,480	n.a.	---
S ²⁻ (μg/L)	---	465	---	36	52	36	-429	n.a.	69.4
Al (FI) (μg/L)	69	90	---	29	---	---	---	n.a.	---
Al (FI) (μg/L)	---	595	45	39	---	39	-556	n.a.	---
Al (UI) (μg/L)	---	6.3	---	12.9	---	8.4	+2.1	n.a.	17.2
Fe (FI) (μg/L)	---	60	---	---	---	---	---	n.a.	---
Fe (UI) (μg/L)	---	6.1	---	2.01	---	2.02	+1.4	n.a.	7.69
Mn (FI) (μg/L)	7.7	4.3	2.7	2.6	2.5	2.6	-1.7	n.a.	---
Mn (UI) (μg/L)	---	30	---	27	---	810	+780	n.a.	---
As (V) (μg/L)	---	1,420	1,505	1,520	1,540	1,615	+135	1.09	---
As (V) + As (III) (μg/L)	---	73	---	---	---	---	---	n.a.	---
Sb (μg/L)	---	81	---	---	---	---	---	n.a.	---
P ²⁻ (μg/L)	---	2	5	---	---	3	---	n.a.	---

*Filtered samples, except as noted. Stations 2 and 4 were unfiltered.

¹FI = Filtered and field extracted; FI = filtered and lab extracted; UI = unfiltered and lab extracted.

²Concentration at station 5 minus that at station 1.

³Concentration ratio of station 5 to station 1, 1 to 1.

⁴Temperature variation in response to discharge periodicity was measured at selected stations only.

⁵Not applicable.

⁶Soluble reactive phosphorus as P (Strickland and Parsons, 1968.)

independent (hence additive) in reckoning the total uncertainty in solute concentration at any point along the drainage channel.

STATISTICAL DEFINITIONS

Let $R(S)_{ij}$ be the ratio R of concentration for solute S at stations i and j , respectively, along a drainage channel. Let $R_i(S)$ be the ratio where the base station $j = 1$. For mixed water systems, let $P_i(S)$ denote the fraction of water at station i which is contributed by source 1 calculated (equation 2) using the conservation of mass principle for solute S (equation 3):

$$P_i(S) = (C_i - C_2) / (C_1 - C_2) \quad (2)$$

$$P * C_1 + (1-p) * C_2 = C_i, \quad (3)$$

where C denotes the concentration of solute S , and p is the mixing fraction.

OCTOPUS AND AZURE SPRINGS

OXIDATION AND DIFFUSION PROCESSES

Several oxidative and diffusion-controlled processes have been identified in these two Lower Geyser Basin hot-spring drainages (figs. 3 and 4). Oxygen concentration and Eh increase with station number because of oxygen diffusion from the atmosphere into the cooling turbulent flow; pH increases 1 to 2 units, presumably

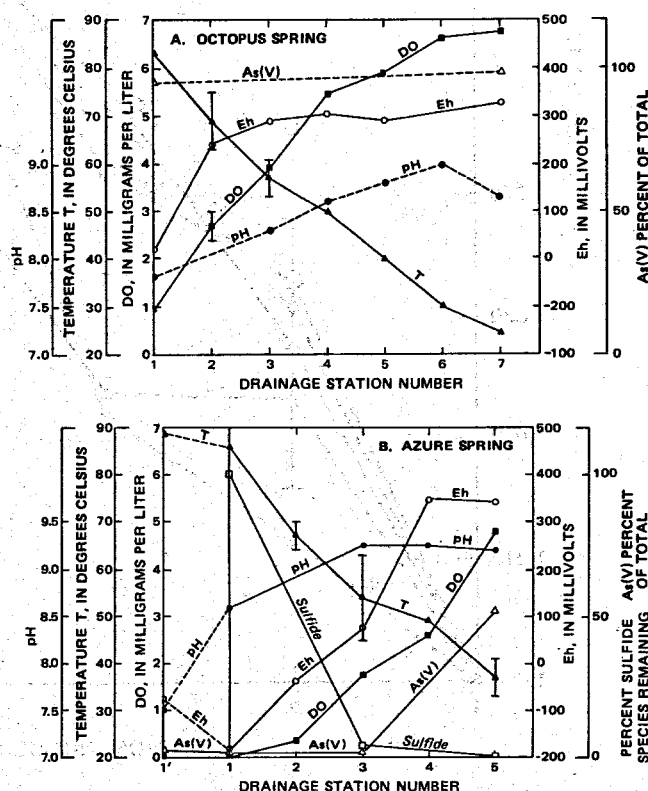


FIGURE 3.—Physical and chemical parameters of two hot springs and their drainages. (Vertical bars on curves represent the range in observed values. Sulfide was below detection in Octopus Spring.)

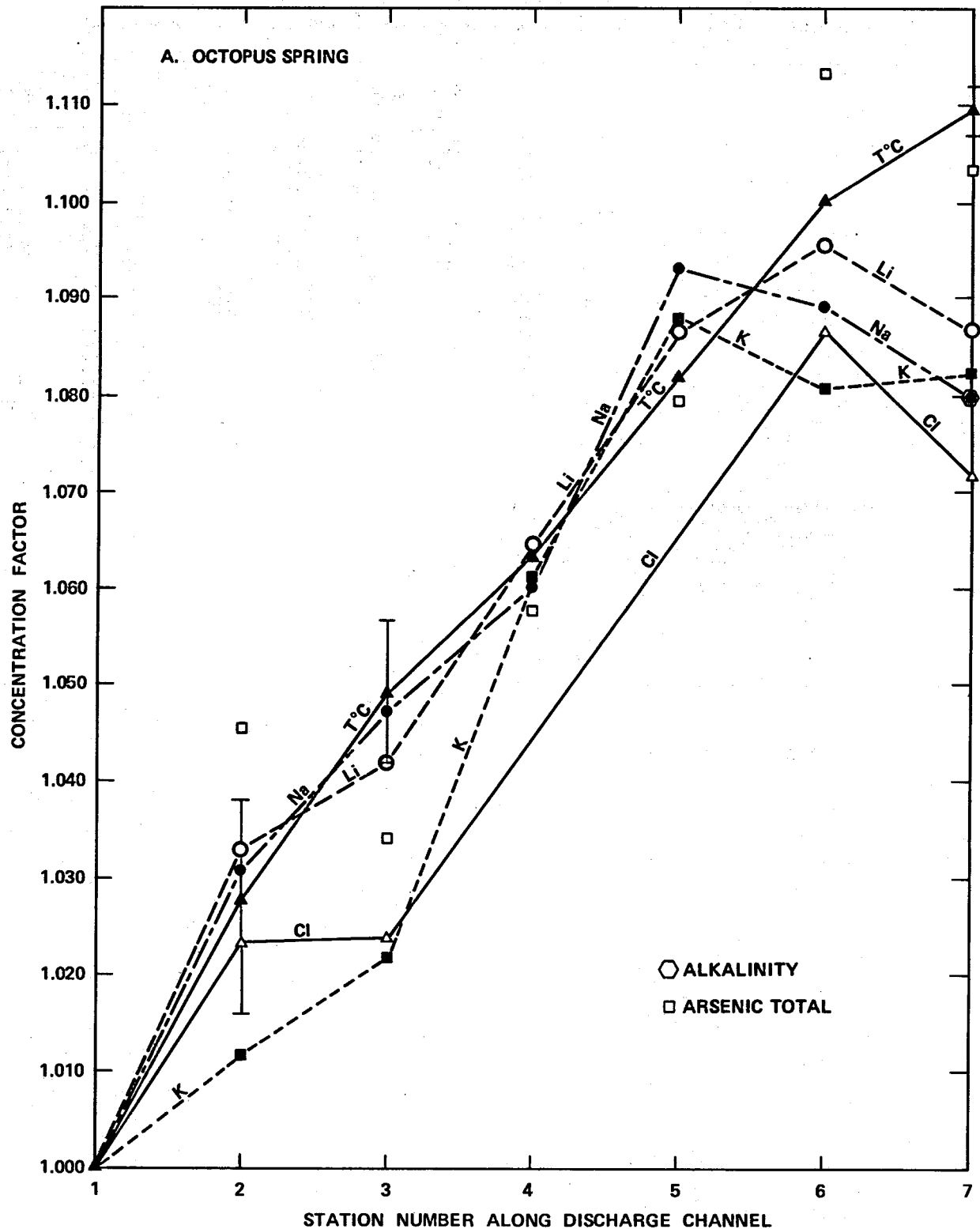


FIGURE 4.—Concentration factors of several parameters for two hot springs and their drainages. (The vertical bars on the T curves represent limits on the concentration factors which are attributed to the observed temperature range. The concentration factors for the satellite pool in figure 4B are inverted to economize on graphical representation).

because of CO_2 losses accompanying evaporative cooling. Analytical dissolved O_2 concentrations in the upper channels are particularly sensitive to discharge

fluctuations because gaseous diffusion is sensitively related to water temperatures, turbulence, and residence time in the channel.

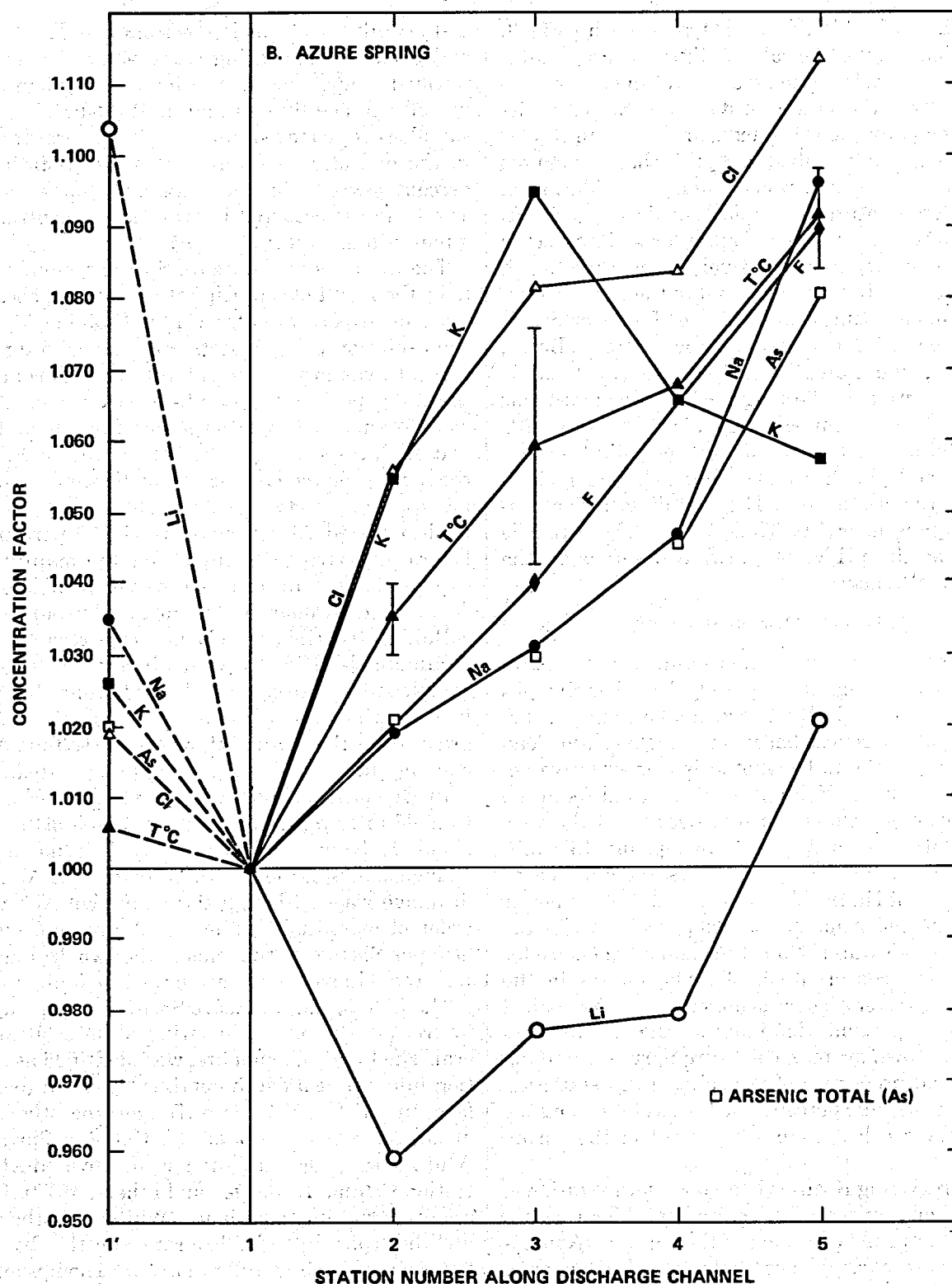


FIGURE 4.—Continued.

If dissolved O_2 is detectable by Winkler titration, S(-II) is below detection, Eh is positive, and the As(III)/As(V) ratio is much less than 1 (figs. 3, 4). Conversely, the presence of analytically detectable S(-II)

implies near-zero dissolved O_2 levels, negative Eh values, and large As(III)/As(V) ratios (in some cases >50). Arsenite (As(III)) is not oxidized in significant quantities until after the S(-II) has been either volatilized

or oxidized. The S(-II)-dissolved O_2 relationship (fig. 3) suggests that at 90°C the rate of diffusion of molecular O_2 into the hot pools is the rate-controlling step in the oxidation of S(-II). Traces of dissolved S(-II) sometimes accompany nonzero oxygen levels in cooler down-drainage water (tables 2, 3); this thermodynamic disequilibrium probably reflects delayed oxidation at the lower temperature. The abiotic oxidation of S(-II) is known to be approximately first order with respect to both S(-II) and O_2 , to be relatively insensitive to pH, and to be relatively slow compared to the expected hydraulic residence times (minutes) in the lower drainage channels (O'Brien and Birkner, 1977). Brock, Brock, Bott, and Edwards (1971) noted that sulfur bacteria are active in oxidizing S(-II) (using molecular O_2) even at boiling temperatures (approximately 92°C on the Yellowstone plateau) in the alkaline hot springs. Some H_2S volatilizes from the channels, yielding the characteristic odor. The first dissociation constant of H_2S is near 7.0. Thus, H_2S volatilization is decreased at the pH values near 8 observed in the lower channel reaches.

PRECIPITATION REACTION

The hypothesized evaporation-solute concentration model (T curves in fig. 4) adequately describes changes in F, Cl, As, and Na in the two drainage channels (fig. 4). Statistical inferences based on the $R(S)$ ratios lead to acceptance of the null hypothesis (conservative behavior) for Na, K, Li, F, alkalinity, and total As in the downdrainage of Octopus Spring. Because of the very high concentrations of Na in Azure Spring (13.5 millimolar) relative to other constituents, the anticipated low reactivity of Na in this situation, and the superior analytical precision for Na as compared to Cl in the high- SO_4 , high-F water, Na is the element of choice for evaluating the conservatism of other solutes in the Azure Spring system. There is no convincing statistical evidence of As precipitation in either the satellite pool or along the down drainage of Azure Spring. Applying the statistical properties of the solute ratio statistics, with probability ~95 percent, the losses of As along the drainageway are less than 1.8 percent of the spring flux.

The Azure Spring K ratios increase prior to station 4, as expected of a conservative solute, and then decrease significantly in the latter part of the channel. Approximately 95-percent confidence limits on the K losses prior to station 5 are 3.5 ± 0.9 percent, or 0.48 mg/L of K.

Li is nonconservative in the Azure Spring system. A 7.5 percent loss of Li is indicated prior to station 2 of the downdrainage and an 8 percent loss in the satellite as compared to the main upwelling pool (fig. 4). After station 2, the Li ratios increase at a rate which is not

statistically distinguishable from the T, Cl, Na, As, and F curves, indicating conservative behavior after initial Li deposition in the immediate vicinity of the upwelling. The filtered and unfiltered HNO_3 -acidified sample sets yielded similar results (8 percent loss of Li in the downdrainage, all of it prior to station 3; 9½ percent low concentration anomaly in the satellite). The Li losses occurred in two sharply contrasting regimes of temperature and pH.

The Li losses in the Azure Spring system are likely to be the result of coprecipitation with Al, because 430 $\mu g/L$, or 92 percent of the original soluble Al, was lost from solution prior to station 3 and >395 $\mu g/L$, or 85 percent, was lost in the satellite pool as compared to the main pool. Total (solute + suspended) Al losses were 525 and 555 $\mu g/L$ in the satellite pool and prior to station 3, respectively. The field-extracted Al data for the main pool and channel show the same trend as the laboratory-extracted Al data (table 3); however, the field-extracted Al estimate is only 19 percent of the laboratory-extracted estimate for the main pool. One explanation for this contrast is that the field-extracted Al (filtered through a 0.1 μm membrane) includes a colloidal fraction which is not extractable with 8-quinolinol-MIBK but which becomes soluble during sample storage at pH ≈ 1 . The difference between the field- and laboratory-extracted soluble Al estimate is greatest for the main pool, where the soluble Al is presumably in the process of being precipitated.

In Octopus Spring the field-extracted Al decreases from 47 to 16 $\mu g/L$, concomitant with a pH increase of about 1, between stations 1 and 7; no significant change occurs in the laboratory-extracted Al along the drainage way. Although the main pool Al level is an order of magnitude higher for Azure as compared to Octopus Spring, at the ends of the two drainage channels the Al levels have converged to similar values.

The Li losses in the Azure Spring system may be due to precipitation of a Li-bearing aluminosilicate mineral. The Li mica, lepidolite, was identified as a deposition mineral at a depth of 25–40 m (below surface) in the Y-3 drill core (Barger and others, 1973), about 75 m northwest of Ojo Caliente Spring. Like Azure Spring, Ojo Caliente has an elevated Al concentration (1.0 mg/L, Barger and others, 1973). Both the scientific drilling experience (White and others, 1975) and the typically high Cl/Li ratios for the River Group hot springs (R. E. Stauffer and J. M. Thompson, unpub. data, 1975) suggest that Azure Spring and Ojo Caliente are derived from a common hot-water upflow regime where Li is being precipitated in the epithermal zone.

If lepidolite is, in fact, forming in Azure Spring, the Li losses are probably not confined to the formation of this mineral. The Al/Li molar loss ratio for Azure

Spring is estimated to be 0.42, in contrast to the ratio 1.27 for lepidolite found by Barger, Beeson, Fournier, and Muffler (1973). Furthermore, the stoichiometry of lepidolite ($K_2Li_3Al_3(AlSi_3O_{10})_2(OH F)_4$) calls for K losses in the Azure Spring system twice as large as those inferred from figure 4.

The concentrations of Mn and Fe in Azure and Octopus Spring waters are representative of the very low levels of these two elements in typical alkaline high-Cl (>250 mg/L) hot springs in the Upper, Lower and Norris Geyser Basins (tables 4 and 5). Significantly, water collected from the base of Porcelain Terrace at Norris has the lowest levels of both Fe and Mn of all the waters tested; this spring also has the highest Cl level, hence the minimum dilution of hot-spring water, in Yellowstone Park. Ear Spring, representative of the high-Cl, low- HCO_3 waters of Geyser Hill, Upper Basin, also features low levels of both Fe and Mn. An unnamed spring north of the Old Faithful interchange is a warm spring formed by near-surface dilution of hot high-Cl water with meteoric water. By contrast, this diluted spring has relatively high levels of both Fe and Mn. Steady Geyser is a dilute (low-Cl) hot spring in the Lower Basin characterized by low Fe levels and a large Mn/Fe ratio (table 5). The elevated Mn/Fe ratio indicates preferential oxidation of Fe(II) and losses from solution following dilution near surface waters. Little Whirligig water is a mixture of high-Cl, low- HCO_3 Norris deep water with acid-sulfate water (low-Cl) of surficial origin. The acidic pH of the mixture preserves the relatively high levels of both Fe and Mn and the small Mn/Fe ratio to be expected from leaching of country rock by the acid-sulfate water component. Brock,

TABLE 5.—Chloride, aluminum, iron, and manganese in selected geysers and hot springs

Sample	Source	Cl (mg/L)	Al (μg/L)	Fe (μg/L)	Mn (μg/L)
Upper Basin:					
YT-73-71	Ear Spring, Geyser Hill	*403	<5	1.1	1.0
YT-73-62	Sapphire, Biscuit Basin	*297	7	7.9	.9
YT-73-76	Excelsior, Midway Basin	*266	23	1.5	18.3
74WA122U ¹	Seep near Old Faithful	365	45	24	1.3
74WA123U	Tortoise Shell	389	26	2.4	.5
74WA124U	Unnamed, largest geyser near Sawmill	382	56	6.7	.5
74WA125U	Witches Cauldron	377	27	1.6	1.2
74WA126U	Unnamed, east of Old Faithful, across Firehole River	272	<6	5.2	1.5
74WA127U	Spouter	317	29	3.5	.7
74WA128U	Unnamed, new, below Old Faithful Interchange	242	16	154	14.3
74WA129U	Unnamed, Black Sand Basin	314	23	64	7.4
74WA130U	Unnamed, north of Old Faithful Interchange	353	36	20	1.4
Lower Basin:					
YT-73-68	Gentian, Fountain Group	*300	11	2.7	.7
YT-73-69	Steady, at Firehole Lake	*46	11	5.1	54.7
Norris:					
YT-73-61	Little Whirligig	*587	10	160	20.8
YT-73-74	Base of Porcelain Terrace	*704	<5	<.7	.4
Mammoth:					
YT-73-65	New Highland	*166	6	7.9	15.0
74WA146U	New Highland	171	18	7.1	15.8
74WA147U	Unnamed, new, blue colored near New Highland	166	53	14.3	12.7

*Chloride analyses by J. M. Thompson on HNO_3 acidified samples.

¹The letter U following the sample number indicates these samples are unfiltered; the other samples were filtered.

Cook, Peterson, and Mosser (1976) have found pure "acid sulfate type" (White, 1957; White and others 1971) thermal waters in Gibbon Meadows and Norris Basin with total soluble Fe levels (Fe(II) and Fe(III)) exceeding 50 mg/L.

UNNAMED SULFIDE-BEARING SPRINGS IN YELLOWSTONE CANYON

Generically, both the 46°C source waters in the unnamed sulfide-bearing spring system in Yellowstone Canyon would be classified as "warm" springs of

TABLE 4.—Selected physical and chemical properties of additional hot waters

[Temperature, E_h , and O_2 are field determinations; other analyses performed after return to Menlo Park Laboratory]

Sample	Source	Temperature (°C)	E_h (mV)	O_2 (aq) (mg/L)	S(-II) (μg/L)	As (V) + As (III) (μg/L)	As (V) (μg/L)	As (III) (μg/L)	As (III)/As (V)
Lower Geyser Basin:									
74WA119	White Creek ¹	51	274	---	---	345	315	~30	0.10
Upper Geyser Basin:									
74WA122U	Seep near Old Faithful	89.5	-170	.0	630	1,280	≤35	~1,245	≥35
74WA123U	Tortoise Shell	93.5	-156	.0	550	1,620	≤30	~1,590	≥53
74WA124U	Unnamed, largest geyser near Sawmill	89.5	-37	.22	<15	1,590	~1,260	~330	.25
74WA125	Witches Cauldron	91.0	-108	.0	150	1,500	≤40	1,460	≥36
74WA126U	Unnamed, east of Old Faithful across Firehole River	87	---	.0	390	850	≤20	~830	≥41
74WA127U	Spouter, Black Sand Meadow	85	-116	.0	190	1,495	≤70	~1,425	≥20
74WA128U	Unnamed, new, below Old Faithful Interchange	73.5	+185	.60	<15	895	860	~35	.04
74WA129U	Unnamed, Black Sand Meadow	88.5	-109	.0	90	1,455	≤280	>1,175	>4.2
74WA130U	Unnamed, north of Old Faithful Interchange	82	---	.0	130	1,255	≤200	>1,055	>5.3
Mammoth:									
74WA146U	New Highland ¹	---	---	---	---	690	≤15	≥675	>45
74WA147U	Unnamed, new blue-colored, near New Highland ²	---	---	---	---	680	≤70	≥610	>9

¹Filtered sample; the other samples are unfiltered.

²On HNO_3 -acidified samples.

"mixed" origin (see Fournier and others, 1974; Fournier and Truesdell, 1974; Fournier and others, 1976). The intermediate Cl levels and high HCO_3^- , Mg, and Ca concentrations (table 6) identify the two source waters as high-Cl, high-enthalpy deep water which has been extensively diluted by meteoric water and has reacted with underlying carbonate rock strata. The high S(-II) and SO_4 concentrations of the springs, and the extensive solfataric activity in the surrounding region of the Yellowstone Canyon, may have their explanation in hot water leaching underlying sulfur-rich sedimentary rock. Similar conditions also exist in the Mammoth area, where some warm springs have reduced Cl levels and concentrations of major constituents which resemble the 46°C source water studied here (Rowe and others, 1973).

The low F levels and high Cl/F ratios in the Yellowstone Canyon Springs (derived from data in table 6) probably result from fluorite equilibria acting on these high-Ca waters (Mahon, 1964; Nordstrom and Jenne, 1977).

The sharp increases in pH, Eh, and dissolved O_2 concentration below the confluence and the decreases in S(-II) reflect gas exchange (CO_2 , H_2S) with the atmosphere and S(-II) oxidation, respectively. The high-carbonate alkalinity of these waters dominates the pH despite the release of protons accompanying S(-II) oxidation.

Inferences based on the solute mixing fraction statistics $P(S)$ (equation 3) must account for the solute-

specific variances. The Li and K statistics are the most precise because of the large concentration differences between the two source waters for these two elements, and the high analytical precision at the concentration levels analyzed. The high SO_4 concentrations increase the analytical c.v. for Cl to ~2.5 percent. The large SO_4/F equivalence ratio insures adequate analytical precision for the SO_4 statistics. However, the high concentrations of S(-II) species in the source 1 water, and their potential for oxidation to SO_4 , add uncertainty to the SO_4 statistics. The $P(F)$ statistics are imprecise because of the low F concentrations and small concentration difference between the two source waters. The precision and accuracy of the $P(\text{As})$ statistics in this system suffer from the relatively high P concentrations, and the high and variable levels of S(-II) species among the samples (Stauffer, 1980b).

The $P_3(S)$ (subscript identifies station) for S(-II), Cl, Na, K, and Li are statistically equivalent. The $P_4(S)$ statistics for these four solutes are all significantly smaller than the $P_3(S)$ values, indicating that the water sample obtained from immediately below the confluence was biased in favor of source 1 water. The sampling bias reflects incomplete mixing of the two source waters. The steep gradient and adequate mixing length between stations 3 and 4 insure that $P_4(S)$ values are unbiased (best estimate $P_4 = 0.375 \pm 0.007$). The equivalence of the Cl, Na, K and Li mixing-fraction statistics indicates conservative behavior for the three alkalis in this system. Because of the high

TABLE 6.—Chemical and physical parameters of Calcite and two other unnamed sulfide-bearing springs in Yellowstone Canyon with the drainage of the mixed spring system

[Temperature, Eh, pH, and O_2 are field determinations; other analyses performed after return to Menlo Park Laboratory, except as noted]

Parameter ¹	Calcite spring	Stations along common discharge drainage of two unnamed springs ^a					Mixing fraction ²		Concentration ratio ³ (5/4)
		Spring	1	2 Spring	3	4	5	$P_3(S)$	$P_4(S)$
Sample 74WA	144	142	141	143	140	139	138		
Time (hr)	1,700	~1,400	~1,300	~1,500	~1,215	~1,130	~1,030	n.a.	n.a.
Temperature (°C)	90	46	40	14	23-26	19	14.5	n.a.	n.a.
pH	7.72	5.98	6.90	7.45	7.22	8.05	8.35	n.a.	n.a.
Eh(mV)	-166	-94	-66	+14	-30	+185	+139	n.a.	n.a.
$\text{O}_2(\text{aq})$ (mg/L)	0	0	0	4.60	.80	5.10	5.80	n.a.	n.a.
Alkalinity	261	798	~600	207	399	399	399	n.a.	n.a.
Na (mg/L)	196	---	116	36.6	75.3	63.0	64.8	.487	.333
K (mg/L)	95.8	---	56.4	14.1	34.8	29.9	29.5	.489	.374
Li (mg/L)	2.24	---	1.09	.22	.65	.54	.56	.495	.368
Mg (mg/L)	12.6	28.5	29.1	16.4	21.4	19.4	20.3	.394	.236
Ca (mg/L)	28.2	227	232	62.0	141	120	123	.465	.341
SO_4 (mg/L)	203	251	279	86	187	159	171	.523	.378
Cl (mg/L)	242	112	127	25	78	64	63	.487	.382
F (mg/L)	4.3	2.2	2.5	1.6	2.0	2.0	2.0	.550	.470
SiO_2 (mg/L)	169	72	78	68	68	69	66	n.a.	n.a.
S^{2-} (μg/L)	2,800	3,210	4,800	55	2,250	<15	<15	n.a.	n.a.
Al (FI) (μg/L)	113	239	243	11	128	94	12	n.a.	n.a.
Al (FI) (μg/L)	---	328	415	<4	69	---	<4	n.a.	n.a.
Fe (FI) (μg/L)	3.5	190	215	35	113	108	6	n.a.	n.a.
Mn (FI) (μg/L)	7.4	283	98	89	88	88	37	n.a.	n.a.
As(V) + As(III) (μg/L)	1,450	742	710	150	395	280	270	n.a.	n.a.
Sb (μg/L)	54	---	---	---	---	---	---	---	---
P (μg/L)	2	61	57	57	53	56	60	n.a.	n.a.

¹Filtered sample, the other samples are unfiltered.

²FI = filtered and field extracted; FI = filtered and lab extracted; UI = unfiltered and lab extracted.

³ $P_3(S)$ is defined as the apparent fraction of water at station 3 which is source 1 water; similarly, $P_4(S)$.

⁴Concentration ratio of station 5 to station 4.

⁵Not applicable.

⁶Best estimate; sample poorly mixed.

⁷Soluble reactive phosphorus as P (Strickland and Parsons, 1968).

K/Al atomic ratio (93 for source 1, higher for source 2) and the very short hydraulic residence time in the system, the conservation of K is to be expected. The mean mixing fractions (\bar{P}_3, \bar{P}_4) for the conservative elemental suite (Na, K, Li, Cl) are used to quantitatively evaluate the behavior of Ca, Mg, Al, Fe, Mn, As and P in the mixed-water system.

The concentrations of Mg and Ca recovered at stations 4 and 5 indicate minor losses of both elements below the confluence (1.3 mg/L Mg, or 6 percent; 6 mg/L Ca, or 5 percent). Temperature-dependent mineral equilibria calculations performed using WATEQF (Plummer and others, 1976) revealed supersaturation with respect to carbonate and silicate minerals at station 4. The saturation indices ($I_s = \log_{10} (IAP/KT) *$ at station 4 were: calcite ($I_s = 1.07$); magnesite ($I_s = 0.25$); and well-ordered sepiolite ($I_s = 0.35$). The pH increase and temperature decrease below station 4 (table 6) result in increased supersaturation with respect to sepiolite at the lower station. Neighboring boiling "Calcite" spring is also strongly supersaturated with respect to both well-ordered and poorly ordered sepiolites ($I_s = 4.22$; $I_s = 2.63$). The "Calcite" spring was near saturation with respect to calcite ($I_s = -0.14$) and magnesite ($I_s = 0.37$).

The Yellowstone Canyon thermal springs are also supersaturated with respect to a broad class of aluminosilicates, especially the montmorillonites. Clearly, the potential exists for Ca and Mg solute losses via a variety of mineral reactions. However, because of the great stoichiometric excesses of Mg and Ca over Al in these springs, carbonates and pure silicates are likely to be the more important solubility controls. Wollast, MacKenzie, and Bricker (1968) noted that the

precipitation of sepiolite is not kinetically hindered at low temperatures (25°C).

Field-extractable soluble Al decreased rapidly below the confluence (table 7), whereas laboratory-extractable Al did not show a decrease until at least station 4, continuing the lag pattern noted earlier for the Azure Spring drainage channel.

Iron precipitation in the drainage (table 7) likely results from at least two mechanisms: amorphous FeS deposition from the high S(-II) waters accompanying the rapid pH rise, and Fe precipitation as amorphous hydrous oxide from the oxygenated waters as they attain positive Eh values (Hem, 1977). Large quantities of black precipitate (presumed to be FeS) were observed above station 3 in the mixed water, and especially above the confluence in the source 1 tributary. Reddish-brown hydrous oxide coatings were abundant in the drainage channel of the oxygenated 14°C source. The oxidation of both Fe(II) and S(-II) is probably mediated by the luxuriant growths of white filamentous bacteria observed in the drainage channel above station 4 (Castenholz, 1973). Calculations using WATEQF confirmed supersaturation with respect to amorphous FeS at station 1 ($I_s = 0.90$) and with respect to amorphous Fe(OH)₃ at station 4 ($I_s = 2.12$).

Soluble Mn and Fe concentrations were characterized by minor losses prior to station 4 and losses of 60 and 95 percent, respectively, by station 5 (table 7). The increases in the Mn/Fe ratio with distance below the confluence indicate a less rapid oxidation rate of Mn(II) than of Fe(II) in the aerated water. Singer and Stumm (1970) discussed the enormous kinetic enhancement of Fe(II) oxidation associated with bacterial oxidation. The rate of oxidation of Mn(II) increases with increasing pH and increasing MnO₂ surface area, a catalytic effect (Morgan, 1967; Delfino and Lee, 1968). The observed delay in oxidation of Mn(II) and

*IAP/KT is the ratio of ion-activity product to thermodynamic solubility constant.)

TABLE 7.—Estimated solute losses following mixing in Yellowstone Canyon mixed spring and Madison River systems

Constituent	Projected concentration at confluence ¹	Station 3 ²			Station 4			Station 5		
		Concentration found	Loss from confluence		Concentration found	Loss from confluence		Concentration found	Loss from confluence	
		(μg/L)	(μg/L)	(percent)	(μg/L)	(μg/L)	(percent)	(μg/L)	(μg/L)	(percent)
Yellowstone Canyon mixed springs:										
S (-II)	1,782	---	---	---	0	1,782	100	0	---	---
Al (FO) ³	151	---	---	---	94	1	1	<4	151	100
Al (FI)	95	---	---	---	12	83	87	12	83	87
Fe (FI)	101	---	---	---	108	-7	-7	6	95	95
Mn (FI)	92	---	---	---	88	4	4	37	55	60
As ⁴ + As ⁵	354	---	---	---	280	74	21	270	84	24
P ⁴	57	---	---	---	56	1	2	60	-3	-5
Madison River system:										
Al (FO)	106	67	39	37	56	50	74	62	44	42
Al (FI)	102	111	-9	-9	97	5	5	90	12	12
Fe (FI)	18	16	2	11	13	5	28	14	4	22
Mn (FI)	8.5	7.6	.9	11	5.8	2.7	32	1.6	6.9	81
As (V) + As (III)	206	212	-6	-3	200	6	3	204	2	1
P ⁴	5.4	6	-6	-11	8	-2.6	-37	2	3.4	63

¹Computed from source waters using mean mixing fractions for Na, K, Li and Cl from tables 6 and 8.

²Station in Yellowstone Canyon Mixed Spring System omitted due to nonrepresentativeness of collected sample.

³FF = filtered and field extracted; FI = filtered and lab extracted.

⁴Soluble reactive phosphorus as P (Strickland and Parsons, 1968).

hence the increase in the Mn/Fe ratio down drainage fits the Mn oxidation model.

The relatively low concentrations of S(-II), Fe, and Al found at station 2 (14°C source) are probably residuals of higher concentrations prevailing before interaction with the atmosphere. The high Mn/Fe ratio for source 2 is also evidence of the delayed oxidation of Mn(II) relative to Fe(II).

Soluble reactive P shows no statistical evidence of precipitation losses below the confluence. Whereas Fe(II) and S(-II) are potential energy substrates for the filamentous bacteria in the channel, P is used only for steady-state maintenance of the bacterial population. The precipitation of $\approx 102 \mu\text{g}$ of Fe/L between stations 4 and 5 did not result in a significant reduction in P or As concentration. The high pH (>8.0) is unfavorable for P and As(V) sorption on hydrous ferric oxides (see later discussion). An estimated 2 percent of the total solute As was lost between stations 4 and 5, the region where the principal losses of Fe and Mn through oxidation occurred. The As loss is not statistically significant.

MADISON RIVER SYSTEM

The date/time group is different for each of the sampling sites in the Madison River system. Time of day can be expected to affect temperature, pH, and dissolved O_2 at a site because of diurnal effects of the solar cycle on heating and photosynthesis. The estimated fraction of Madison River water at station 3, which is derived from the Firehole River and calculated using solute concentrations (equation 2), is biased unless the solute concentrations were independent of time during September 18–21. Because the period September 18–21 was precipitation free for the water, and was a low-flow period for the Madison River, the assumption of time independence in solute concentrations is equivalent to assuming that the cold-spring and hot-spring fluxes in the Gibbon and Firehole River drainages were invariant during the 3-day span. One indication of the near correctness of that assumption is provided by the close comparisons (mean difference <2 percent) in two sets of total As data for stations 1 and 2, collected 11 to 14 days apart during late September-early October 1974. The steadiness of the geothermal solute flux over short timespans has been noted by others (Fournier and others, 1976).

The best estimate of the Firehole River mixing fraction P_3 (fraction of Madison River discharge at station 3 derived from the Firehole Tributary) lies in the interval 0.70 to 0.75 (table 8). The geothermal indicator element, Li, defines the fraction most precisely because of the high analytical precision and the large concentration difference between the two tributaries.

The $P_3(\text{As})$ value, 0.76, indicates that As being transported in the Gibbon and Firehole Rivers remains in solution below the confluence and above station 3.

Using solute concentration ratios defined analogously to those for the Lower Basin, the geochemical behavior of Li and As can be contrasted with that of Cl in the Madison Canyon region. Let $R_{i/3}(S)$ where $i = 4, 5, 6$, be the ratio of solute S concentration at station i to the concentration at station 3, immediately below the confluence. The $R_{4/3}(S)$ and $R_{5/3}(S)$ ratios apply to the Madison River between West Yellowstone and Madison Junction. The $R_{6/3}(S)$ ratios reflect the extensive dilution of Madison River water by stored water and other tributary water flowing into Hebgen Lake. Additions of geothermal water between Madison Junction and West Yellowstone are considered here to be negligible. This assumption is only approximately correct; however, inferences based on the solute ratio statistics are rather insensitive to minor unaccounted geothermal fluxes within Madison Canyon.

Elements which are well represented in nonthermal waters (particularly K, Ca, and Mg) can be expected to have R_4 , R_5 and R_6 ratios higher than for Cl. This was, in fact, observed (table 8). The $R_{4/3}$ and $R_{5/3}$ ratios for K, Ca, and Mg are only slightly higher than for Cl because of the very slight tributary development of the Madison River within the Madison Canyon. The $R_{5/3}(\text{Cl})$ statistic shows that the water at Madison Junction has been diluted by approximately 5 percent when it arrives at West Yellowstone gaging station.

Elements of geothermal origin which behave conservatively in the river will have concentration ratios which are not statistically distinguishable from the Cl ratios. Nonconservative behavior is identifiable by concentration ratios significantly lower than for Cl. Thus, the concentration ratios indicate that both Li and total As are conservative in the Madison Canyon (table 8). The mean percent difference between the As/Cl and Li/Cl ratios for stations 4 and 5 is only -0.3 percent. A -2.0 percent mean difference between the As/Cl ratios, or between the Li/Cl ratios, is necessary to reject the null hypothesis (equivalent) at the 5 percent level. The statistical test is thus capable of discerning an ~ 2.0 -percent loss of either Li or As in the Madison River above West Yellowstone.

The R_6 ratios for Cl, As, and Li also show quite close agreement (table 8). Because the Cl concentration at station 6 was determined by a different analytical method and different analyst, the Cl ratio has an additional error component. Furthermore, the analytical coefficients of variation for As and Li increase at the low concentration levels characteristic of station 6. Hence, the small negative differences between $R_{6/3}(\text{Li})$ and $R_{6/3}(\text{Cl})$ and between $R_{6/3}(\text{As})$ and $R_{6/3}(\text{Cl})$ are

TABLE 8.—Chemical and physical parameters of the Madison River drainage

[Temperature, Eh, pH, and O₂ are field determinations; other analyses performed after return to Menlo Park Laboratory, except as noted]

Parameter ¹	Stations along Madison River drainage*						Mixing fraction F ₂ (S) ²	Concentration ratio ³	
	Firehole	Gibbon	Madison					5/3	6/1
	1	2	3	4	5	6			
Sample 74WA	107	108	109	110	111	120	---	---	---
Time	1,030	1,230	1,600	1,730	1,400	1,600	n.a. ⁴	n.a.	n.a.
Date (1974)	9/18	9/18	9/18	9/18	9/19	9/21	---	---	---
Temperature (°C)	15.0	14.0	18.5	18.5	16.5	14.0	n.a.	n.a.	n.a.
pH	8.40	7.04	7.50	7.68	8.25	---	n.a.	n.a.	n.a.
Eh (mV)	452	402	358	394	448	---	n.a.	n.a.	n.a.
O ₂ (aq) (mg/L)	7.60	9.10	8.40	8.15	8.20	---	n.a.	n.a.	n.a.
Alkalinity (mg/L)	106	115	115	108	109	---	.18	.948	n.a.
Na (mg/L)	73.6	55.4	68.1	67.5	66.4	---	.70	.976	n.a.
K (mg/L)	6.75	8.40	7.25	7.15	7.15	4.30	.70	.986	.601
Li (mg/L)	.528	.323	.477	.457	.450	.186	.75	.947	.412
Mg (mg/L)	.483	1.23	.704	.691	.762	1.83	.70	1.08	2.40
Ca (mg/L)	5.24	8.29	6.37	6.04	6.12	11.9	.63	.961	1.94
SO ₄ (mg/L)	10	18	13	12	12	---	.60	.954	---
Cl (mg/L)	54	33	47	45	44	20	.66	.949	.449
F (mg/L)	7.2	4.1	6.4	6.4	6.3	---	.74	.984	n.a.
SiO ₂ (mg/L)	100	75	92	86	87	1	n.a.	n.a.	n.a.
Al (FI) (μg/L)	52	235	111	97	90	15	.68	.811	n.a.
Al (FI) (μg/L)	57	235	67	56	62	---	.94	.910	n.a.
Fe (FI) (μg/L)	14	30	16	13	14	24	.87	.875	n.a.
Mn (FI) (μg/L)	2.6	24	7.6	5.8	1.6	24	.78	.205	n.a.
As(V) (μg/L)	245	92	---	185	---	---	---	---	---
As (V) + As (III) (μg/L)	252	83	212	200	204	88	.76	.962	.431
P ⁵ (μg/L)	6	4	6	8	2	7	---	---	---

*Filtered sample, the others samples are unfiltered.

¹FI = filtered and field extracted; FI = filtered and lab extracted; UI = unfiltered and lab extracted.²P₂ (S) is defined as the apparent fraction of water at station 3 which is source 1 water.³Concentration ratio station 5 to station 3, station 6 to station 3.⁴Not applicable.⁵Soluble reactive phosphorus as P (Strickland and Parsons, 1968).

inconclusive evidence of Li and As losses in Hebgen Lake. The ratio comparisons suggest that only a minor fraction of the soluble Li and As fluxes in the Madison River are lost in Hebgen Lake during fall base-flow conditions. The near conservatism is not surprising since the elevated river water temperature and low suspended-solids load of the Madison should lead to short circuiting through the surface waters of Hebgen Lake. Similarly, Axtmann (1974) noted the near conservatism of total As in the Waikato River and Lake Taupo below Wairakei in New Zealand.

The mean P concentration for the Firehole and Madison Rivers (5.5 μg/L) is typical of low levels found in unpolluted rivers derived from forested drainage basins; the present estimates are smaller by a factor of 20 than the As(V)-biased P data previously reported by Boylen and Brock (1973) and Zeikus and Brock (1972) for the Madison River system.

The field-extracted Al estimates reveal a significant loss of Al immediately following the mixing of the Gibbon and Firehole Rivers (table 7). However, following the pattern described for the other drainages studies, the laboratory-extracted Al data reveal smaller decreases, occurring more slowly as a function of distance below the confluence. The methodological difference may be the result of the formation of nonextractable Al polymers (Smith, 1971), which are depolymerized during storage in 0.1 molar HNO₃. The loss of Al is not accompanied by a detectable loss of Li.

The Gibbon River contains higher Al, Fe, and Mn concentrations than the Firehole River. The concentration of soluble Mn decreases gradually below the con-

fluence to ~1.6 μg/L near West Yellowstone; however, no significant change was detected in soluble iron (table 7). The large increases in Mn, Ca, and Mg concentration (1,400, 94, 140 percent, respectively) between stations 5 and 6 are a result of nonthermal waters entering Hebgen Lake from other drainage areas.

SORPTION CONTROLS ON ARSENIC IN GEOTHERMAL WATERS

Amorphous hydrous Fe oxides are the most efficient As scavengers in the class of amorphous precipitates formed by Al, Fe, and Mn in natural waters (Gulledge and O'Connor, 1973; O'Connor, 1974; Singer, 1974). The almost quantitative removal (>99 percent) of As(V) from neutral to acidic solutions using ferric hydroxide coprecipitation has been the chemical basis of many concentration schemes for analyzing As at low levels in the environment (Portmann and Riley, 1964). Furthermore, it is well known that the sorption affinity of ferric hydroxide for As(V) is greatly reduced under alkaline conditions (Portmann and Riley, 1964; O'Connor, 1974). Trivalent As is inefficiently sorbed at all pH values. For example, Logsdon, Sorg, and Symons (1974) found only about 50-percent removal of As(III) (initially at the 0.3 mg/L level) using a 30 mg/L ferric sulfate dose; the percentage removed was independent of acidity in the pH range 6 to 9. For As(V) (initially at 0.05 mg/L) O'Connor (1974) reported 88 percent removal at pH 8.0 in the presence of 10 mg/L Fe(III).

Al is less effective than Fe at scavenging both As(III)

and As(V), the differences increasing above pH 7.0. Logsdon, Sorg, and Symons (1974) found that 30 mg/L alkali aluminium sulfate (alum) treatments removed about 90 percent of As(V) and 10 percent of As(III) in the pH range 5 to 7. The initial As levels tested were 0.30 mg/L, very similar to the total As concentration in the lower Firehole River. Above pH 7.0, the percent removal of As(V) by 30 mg/L alum declined almost linearly to 15 percent at pH 8.5.

The authors are not aware of quantitative studies on As sorption by MnO_2 . However, in light of the chemical similarity between H_3AsO_4 and H_3PO_4 (the two acids have nearly identical pK values for all three dissociations, Sillen and Martell, 1964), and the inefficiency of phosphate sorption on MnO_2 , Mn may play a relatively minor role in the sorption chemistry of As. As sorption on MnO_2 is likely to be insignificant for two additional reasons: (1) The acid leaching of typical igneous rock solubilizes great stoichiometric excesses of both Fe and Al as compared to Mn; (2) the oxidation and precipitation of Mn is often delayed in geothermal waters until the pH is far too high to effect efficient removal of As(V).

The conservative behavior of total As in Octopus Spring is an expected consequence of the high pH and very high As/Fe atomic ratio of 570. Furthermore, very large As/Fe ratios are typical of alkaline hot springs throughout the major hot-spring basins. In Azure Spring, the initial soluble As/Al atomic ratio is only 1.20, in contrast to the As/Fe atomic ratio of 183. However, Al precipitation occurs prior to station 3 in the drainage channel, and prior to the oxidation of a significant amount of As(III). This oxidation lag can be expected to greatly reduce the effectiveness of As removal by oxidic Al precipitates. Coprecipitation of Al with SiO_2 to form montmorillonite (R. O. Fournier, oral communication, 1975) may also reduce As losses onto oxidic Al in the high-Al springs of the River Group. Thermodynamic calculations indicate Azure Spring is supersaturated with respect to several montmorillonites.

The levels of both P and As in the Yellowstone Canyon warm spring indicate that, even in the presence of anomalously high Fe levels ($\approx 200 \mu\text{g/L}$), the removal of As by sorption is relatively insignificant in this alkaline spring water. The low Fe/As molar ratios, the very large As(III)/As(V) initial ratios, and the rapidly rising pH after the emergence of the spring water at the ground surface all combine to reduce sorption by hydrous Fe oxides as an important mechanism affecting As in the drainages of alkaline hot springs.

As behaves nearly conservatively during the long base flow period (losses <2 percent of flux) in the Madison-Firehole River system. In addition to evi-

dence previously discussed, samples obtained from the Firehole River at Madison Junction and just below Lower Basin (early October 1974) had Cl/As atomic ratios of 466, and 456, respectively. Given the probable analytical errors in the Cl and As determinations and the lag time in sampling, the ratio difference is not statistically significant. The Cl/As atomic ratio in the Firehole River is close to the median ratio for hot-spring groups in the Firehole River drainage (R. E. Stauffer and J. M. Thompson, unpublished data, 1975). Because of inadequate spring flow data, a flow-weighted mean Cl/As ratio for the hot springs in the Firehole River drainage cannot be precisely calculated. Based on Fournier, White, and Truesdell (1976) and the difference between the Upper, Midway, and Lower Basin Cl/As ratios, the Firehole River Cl/As ratio is close to a weighted mean for the springs of the drainage basin.

Near conservatism of As during low flow occurs because of the following factors: (1) The soluble Fe/As ratio is too low to significantly affect As by sorption or coprecipitation; (2) although the suspended solids may be assumed to have surface-active coatings of Fe oxides (Jenne, 1968, 1977), the concentration of suspended inorganic solids in the rivers is low during the low-flow period; (3) the alkaline pH of the river during daylight hours is suboptimal for As(V) sorption on Fe oxides.

During high runoff periods (principally the May-June snowmelt period, Fournier and others, 1976) the pH of the Madison River drops and the riverborne flux of sorption-active clastics increases dramatically. During such periods the increased contact opportunity between As (V) and the amorphous Fe oxide coatings on the particulates might be expected to result in significant losses of soluble As in the Madison River. The most likely sink for sorbed As(V) during spring runoff is the sediments of Hebgen Lake.

The Cl/As atomic ratio for the Gibbon River at Madison Junction is 760, a value significantly higher than the ratios for key indicator springs in both the Gibbon (Cl/As = 400 ± 25) and Norris (Cl/As = 543 ± 11) hot-spring basins (R. E. Stauffer and J. M. Thompson, unpublished data, 1975). The Gibbon and Norris thermal basins constitute most of the geothermal activity in the Gibbon River drainage basin (Fournier and others, 1976). The Cl/Li atomic ratio for the Gibbon River at Madison Junction is 20.1, intermediate among the mean ratios for the Norris (23.8 ± 0.5) and Gibbon (Gibbon Meadows area: Cl/Li = 19.2 ± 1.4 ; Artist Paint Pots: Cl/Li = 16.4 ± 0.4) geyser basins (R. E. Stauffer and J. M. Thompson, unpublished data, 1975). On the basis of the Cl/Li ratios, it is possible to infer that in excess of 50 percent of the Gibbon River Cl flux originates in the Gibbon Geyser Basin. An immediate im-

plication of this inequality is that 60 percent or more of the geothermal As flux in the Gibbon River drainage basin during base-flow conditions is removed by precipitation and sorption processes. The high Gibbon River Cl/As ratio probably results from As(V) sorption on hydrous Fe oxides and oxidic Al above Gibbon Canyon as the river's Cl/As ratio is also elevated in the canyon. Some As may also be precipitated as FeAsO_4 and realgar (AsS) in the acidic spring environments (depending on redox potential). Acid-sulfate waters containing high levels of Fe and Al mix with poorly buffered high-Cl, high-As waters in both the Norris and Gibbon thermal basin (Allen and Day, 1935; White, 1957); the pH of the weakly acidic water rises, and large amounts of Fe and Al precipitate. The mixing of two geochemically distinct water types in the Norris-Gibbon region thus produces conditions which are optimal for the sorption of As(V) on both Fe and Al precipitates. The time delay required for mixing and Fe(II) oxidation (Brock and others, 1976) helps insure that As initially in the form of As(III) has been oxidized to the more readily sorbing As(V).

ARSENIC FLUX OF THE MADISON RIVER

Using the September concentration estimate of 202 $\mu\text{g/L}$ of As and available earlier discharge measurements during September low flow at the West Yellowstone gaging station (12.7 m^3/s , U.S. Geological Survey, 1974; flow measurement was discontinued after 1973), the estimated base flow total soluble As flux for the Madison River is 220 kg/day, 90 percent of which is contributed by the Firehole River. An additional 25 to 30 kg/day of As is precipitated in the Gibbon River drainage basin. Because the September geothermal As flux can be assumed to be representative of the daily flux on an annual basis (Fournier and others, 1976; R. E. Stauffer and J. M. Thompson, unpublished data, 1975), the annual total (soluble + particulate) As flux of the Madison River at West Yellowstone is $\approx 90,000$ kg. It is likely that particulate As deposited in the Gibbon drainage basin is flushed out during peak discharge in May and June and deposited in the sediments of Hebgen Lake.

The annual As flux for the Madison River is less than the flux estimate by Axtmann (1974) for Wairakei (158 metric tons) and the atmospheric As flux estimated for the ASARCO Copper smelter in Tacoma, Wash. (150,000 kg/year, Crecelius, 1975). The Tacoma smelter acquired notoriety as a result of its high As flux (Lawson, 1975). Swain (1949) reported an atmospheric As flux of 22.5 metric tons/day for the Anaconda Smelter at Anaconda, Mont., a value which is nearly 100 times the Madison River flux. The reason for the large discrepancy between the present ASARCO and histori-

cal Anaconda fluxes is unclear; however, the high Anaconda figure applies to a period prior to any pollution abatement, and As is currently recovered as a by-product at the Tacoma plant. Because the smelter As flux is almost exclusively the highly toxic particulate As_2O_3 (Crecelius, 1975), and the Madison River flux is dominantly soluble As(V) at the 200 $\mu\text{g/L}$ level, an important distinction exists between the environmental impacts of the two As sources. At levels above 1 mg/L in drinking water, As is associated with long-term toxicity effects in humans, As(III) being notably more toxic than As(V) (Penrose, 1974).

During low-flow conditions the total As concentration at the Hebgen Dam spillway is about 85 to 90 $\mu\text{g/L}$, or about 75 percent, above the U.S. Public Health rejection limit for municipal water supplies (50 $\mu\text{g/L}$, Environmental Protection Agency, 1972). With increasing distance downriver, this level is presumed to be progressively reduced by dilution and sorption on clastics.

POTENTIAL ECOLOGICAL SIGNIFICANCE OF ARSENIC

The ecological role of As in the microbiological communities of the hot-spring drainages, and in the receiving rivers, is mainly a subject of conjecture. As is known to be oxidized and reduced (between As(III) and As(V)) by microorganisms under a variety of natural conditions (Johnson, 1972; Myers and others, 1973; Pilson, 1974). As is also concentrated by a factor of 5,300 by the dominant macrophyte in the Waikato River (Axtmann, 1974, 1975). However, as Penrose (1974) noted, the concentration factors are likely to be highly dependent on aquatic species, as well as redox state of the As. Nothing is known at present about the As concentration factors for algae and macrophytes inhabiting geothermally derived waters in Yellowstone Park. Because of the chemical similarity between AsO_4^{3-} and PO_4^{3-} , and the importance of P as a critical nutrient for all plant forms, both the low levels of P and the very high As(V)/P ratios for many of the hot springs and receiving waters may be of enormous ecological significance in Yellowstone Park. Limnetic environments enriched in As have become dominated by the relatively tolerant blue-green algae (J. Shapiro, oral communication, 1978), suggesting that the As/P gradients in Yellowstone thermal waters may also act to select blue green. Oceanographers have noted that the As/P atomic ratio approaches 1.0 in the oligotrophic waters of the ocean (Portmann and Riley, 1964; Johnson and Pilson, 1972b). Penrose (1974) has noted that marine fish have relatively high As contents, probably as a result of concentration within the food chain and the effects of the As/P ratio on the phytoplankton. As concentration in phytoplankton is also

the probable cause of the high As concentration in organically rich marine shales (Onishi and Sandell, 1955). In Octopus Spring the As(V)/P molar ratio reaches 350, two orders of magnitude higher than the upper bound ratios likely to occur in the ocean. Even in the Madison River the As(V)/P ratio is about 15.

CONCLUSIONS

1. Soluble Al, Fe, and Mn approach low limiting values of <5.0, 1.0, and 1.0 $\mu\text{g/L}$, respectively, in the least diluted high-Cl waters of the Norris and Upper Geyser Basins. The springs so characterized represent zones of highest enthalpy flux in the park. The levels of Al, Fe, and Mn do not appear to correlate with the presence or absence of dissolved S(-II).
2. The soluble-Mn levels are strikingly elevated (approximately two orders of magnitude) in alkaline springs of "mixed water" origin. These springs include the Mammoth hot springs, Steady Geyser, the unnamed spring north of the Old Faithful highway interchange, and the warm springs in the Yellowstone Canyon. The Mn/Fe atomic ratio is >1 in almost all of the alkaline springs of mixed origin, the ratio tending to increase with temperature.
3. The Mn/Fe ratio increases along the drainage channels of S(-II)-containing springs of mixed origin. The increase in the ratio probably reflects the slower rate of Mn(II) vs Fe(II) oxidation and the less effective solubility controls on Mn(II) at low temperatures.
4. Al precipitates rapidly in the relatively rare boiling springs containing elevated levels of the element. Al precipitation apparently occurs in Azure Spring prior to emergence of the water at the surface; the reaction proceeds virtually to completion at 89°C and pH <7.5.
5. Li, and to a lesser extent K, behave nonconservatively if Al is being precipitated from hot-spring waters. The most likely mechanism of Li removal is through the formation of Li-bearing aluminosilicate minerals.
6. P is present in very low concentrations ($\approx 2 \mu\text{g/L}$) in undiluted hot-spring waters of the Upper, Lower, and Norris Basins. Higher concentrations of P are associated with warm springs of mixed-water origin.
7. The As(III)/As(V) ratio in these thermal waters varies over three orders of magnitude and is strongly bimodally distributed according to whether or not S(-II) is present in detectable quantities.
8. Arsenite is rapidly oxidized to As(V) in the hot-

spring drainages, but only after the volatilization and oxidation of S(-II).

9. Total As is essentially conservative (losses under 2 percent) in all of the surface-water systems studied, with the prominent exception of the Gibbon River. The major losses of total dissolved As in the Gibbon River occur above Gibbon Canyon and are hypothesized to result from As(V) sorption on oxidic Fe and Al formed as a result of the mixing of acid-sulfate and alkaline high-Cl waters in the upper Gibbon drainage basin.
10. The high levels of As, the variable As(III)/As(V) ratios, and the extraordinarily high As/P ratios in Yellowstone geothermal waters are potential adverse ecological factors in the park.

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