

Arsenic and antimony in geothermal waters of Yellowstone National Park, Wyoming, USA

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Abstract—A total of 268 thermal spring samples were analyzed for total soluble As using reduced molybdenum-blue; 27 of these samples were also analyzed for total Sb using flame atomic absorption spectrometry. At Yellowstone the Cl/As atomic ratio is nearly constant among neutral-alkaline springs with Cl > 100 mg L⁻¹, and within restricted geographic areas, indicating no differential effects of adiabatic vs. conductive cooling on arsenic. The Cl/As ratio increases with silica and decreases with decreasing Cl/ΣCO₃; the latter relationship is best exemplified for springs along the extensively sampled SE-NW trend within the Lone Star-Upper-Midway Basin region. The relationship between Cl/As and Cl/ΣCO₃ at Yellowstone suggests a possible rock leaching rather than magmatic origin for much of the Park's total As flux. Condensed vapor springs are low in both As and Cl. Very high Cl/As ratios (>1000) are associated exclusively with highly diluted (Cl < 100 mg L⁻¹) mixed springs in the Norris and Shoshone Basins and in the Upper White Creek and Firehole Lake areas of Lower Basin. The high ratios are associated with acidity and/or oxygen and iron; they indicate precipitation of As following massive dilution of the As-bearing high-Cl parent water.

Yellowstone Sb ranged from 0.009 at Mammoth to 0.166 mg L⁻¹ at Joseph's Coat Spring. Within basins, the Cl/Sb ratio increases as the Cl/ΣCO₃ ratio decreases, in marked contrast to As. Mixed springs also have elevated Cl/Sb ratios. WHITE (1967) and WEISSBERG (1969) previously reported stibnite (Sb₂S₃), but not orpiment (As₂S₃), precipitating in the near surface zone of alkaline geothermal systems.

INTRODUCTION

GEOCHEMISTS HAVE debated whether the arsenic in hot springs is primarily of magmatic origin (ONISHI and SANDELL, 1955; WHITE, 1957) or of rock leaching origin (HAGUE, 1887; ELLIS, 1970). The close geochemical association between Cl and As suggests that if the Cl is primarily magmatic then the As has a similar origin. However, ELLIS and MAHON (1964) showed that rhyolitic pumice could yield substantial As and Cl during 72 hours of leaching by pure water at 310°C. Furthermore, ONISHI and SANDELL (1955) found elevated concentrations of As in rhyolitic rocks, and especially volcanic glasses (>12 mg kg⁻¹), the rocks especially prone to hot water attack (ELLIS and MAHON, 1964).

In the present paper we examine the geographic and geochemical distribution of arsenic and antimony in the thermal waters of Yellowstone National Park (YNP), addressing the following questions:

1) Is the arsenic of magmatic origin? Can any fraction of the arsenic be attributed to rock leaching by the ascending hot water?

2) Is arsenic of diagnostic value in identifying separate enthalpy reservoirs in hot-water dominated systems?

3) What are the conditions for arsenic and/or antimony precipitation in the country rock during fluid migrations?

In attempting to answer these questions we focus particular attention on the distributions of the Cl/As, Cl/Sb, and As/Sb atomic ratios, and their relationships to the Cl/B, Cl/Li, and Cl/ΣCO₃ ratios. The study of statistical patterns in the Cl-based ratios follows the initiatives of ELLIS and WILSON (1955, 1960) and MAHON (1970) who recognized chloride's conservative behavior in solution and the element's fundamental linkage to the high enthalpy parent reservoir(s) feeding hot-water dominated geothermal systems.

METHODS

Sampling

Samples from the thermal springs of YNP, Steamboat Springs, Nevada, and Morgan Springs, Lassen, California were collected during 1966-1975 (principally after 1971) using described procedures (ROWE *et al.*, 1973; THOMPSON *et al.*, 1975; BALL *et al.*, 1976). In the earlier years mainly unfiltered unacidified samples were available. After 1972 field-filtered (0.1 or 0.45 μm pore size) vs. unfiltered, and/or acidified vs. unacidified sample splits have usually been available, allowing comparisons of the chemical effects of field treatments (STAUFFER, 1980a; STAUFFER *et al.*, 1980).

A total of 268 hydrothermal samples were analyzed for As, representing 230 individual springs scattered throughout the most important and accessible thermal basins of YNP (Fig. 1), two samples from Morgan Springs, and five samples from Steamboat Springs. Twenty-seven individual spring

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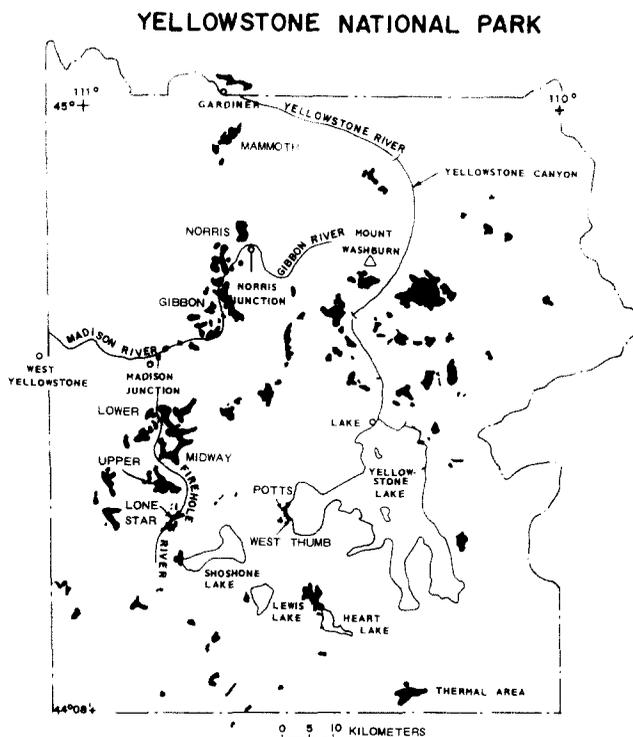


FIG. 1. General locator map for thermal regions of Yellowstone National Park.

samples were analyzed for Sb, representing YNP (23), Morgan Springs (2), and Steamboat Springs (2).

Untreated (by acidification) samples from copious travertine-depositing springs can yield spuriously low As results, possibly because of minor arsenate co-precipitation with calcite (STAUFFER, 1980a; ROTHBAUM and ANDERTON, 1976). Adsorption of As(V) by hydrous Fe(III) oxides in weakly acidic media is a more potent mechanism for removal (PORTMANN and RILEY, 1964; MALOTKY and ANDERSON, 1976).

Fortunately, the typical alkaline high-Cl YNP hot spring water contains low concentrations of Ca because of calcite and fluorite equilibria (STAUFFER, 1982; NORDSTROM and JENNE, 1977) and extremely low concentrations of Fe, Al, and Mn (STAUFFER *et al.*, 1980). The As/Fe atomic ratio typically exceeds 100 or even 1000, hence alteration of the Fe traces accompanying sample storage has no discernible effect on the As. As a consequence, total arsenic determinations on untreated vs. field filtered and acidified samples yield identical results for this large and important class of springs (STAUFFER, 1980a). Even moderately acidic samples from Norris and Gibbon springs of high discharge (for example Little Whirligig and Sylvan) retain comfortably large As/Fe ratios (≥ 5) (*cf.* BROCK, 1978).

Analytical

Arsenic was analyzed using reduced molybdenum-blue (STAUFFER, 1980a), antimony by flame atomic adsorption spectrometry (STAUFFER, 1977), chloride by potentiometric titration (KOLTHOFF and KURODA, 1951), except for 14 samples analyzed by cation exchange (STAUFFER, 1980b), cations by flame atomic absorption spectrometry and boron by the curcumin (APHA, 1971) or carmine (BROWN *et al.*, 1970) procedures. Alkalinity and fluoride determinations followed THOMPSON *et al.* (1975) and STAUFFER *et al.* (1980). All As and Sb analyses were performed by the senior author in 1975.

Chemical speciation of As between arsenite, As(III), and arsenate, As(V), was determined on a small but select group of samples collected in 1974 using more sophisticated sampling apparatus and applying the sample preservation techniques (BALL *et al.*, 1976). These results are reported elsewhere (STAUFFER *et al.*, 1980). All As and Sb results reported here are elemental totals.

For the typical YNP hot spring water with Cl ≥ 250 mg L⁻¹ the analytical coefficient of variation (c.v.) for As $\sim 0.5\%$; the relative bias is $\leq 1\%$. Both the precision and accuracy decrease with decreasing As concentration (STAUFFER, 1980a). The analytical c.v. for Sb is $\sim 10\%$ at the 0.10 mg L⁻¹ level, and changes approximately as the inverse of the concentration. The Cl/As ratio for a typical YNP hot spring has an analytical c.v. $\sim 1\%$; the Cl/Sb and As/Sb ratios have analytical c.v.'s $\sim 10\%$. All elemental ratios are reported in this paper by atoms.

PHYSICAL-CHEMICAL CONDITIONS IN CONVECTING HOT-WATER SYSTEMS

The springs and geysers of YNP are probably derived from superheated Cl-enriched parent waters in the manner depicted by FOURNIER (1979), FOURNIER *et al.* (1974, 1976) and FOURNIER and TRUESDELL (1974). Briefly, upper zone cooling occurs: 1) adiabatically, *i.e.*, boiling; 2) conductively (heat loss to wall rock); 3) by mixing with cold meteoric water; 4) combinations of the above. Only the first two processes, alone or in combination, are considered important on Geyser Hill during fluid migration from the intermediate enthalpy reservoir ($T_r \geq 217^\circ\text{C}$) (FOURNIER *et al.*, 1976). Elsewhere in the park, upper zone cooling (above the intermediate $200^\circ+$ reservoirs) by dilution with meteoric water is a common phenomenon; these springs are exploited in "Mixed-water" geothermometry (TRUESDELL and FOURNIER, 1976, 1977; FOURNIER and TRUESDELL, 1974). Based on enthalpy-chloride relationships, and other evidence, FOURNIER *et al.* (1976) hypothesized that the Geyser Hill

waters (south of Madison Junction) and Norris waters (north of Madison Junction) may be derived from a common primary enthalpy reservoir with a minimum temperature of 337°C. The key high-Cl Norris springs (Pork Chop, Base Porcelain Terrace) may reflect pure adiabatic cooling of this hypothesized 337°C source; the key Geyser Hill waters (Giantess, Old Faithful Geysers) may have first been quenched by meteoric water (to 270°C) enroute to the intermediate enthalpy reservoir, and then cooled adiabatically enroute to the surface.

The various cooling scenarios have different effects on solution pH and redox potential, hence different potential effects on solute As and Sb. Dissolved gases like CO₂, H₂S, and more rarely, NH₃, partition strongly into the vapor phase accompanying boiling, leaving the residual liquid impoverished. Igneous systems are typically rich in the "acidic gases" (CO₂, H₂S) and poor in ammonia, hence the pH rises in the residual liquid accompanying adiabatic cooling. The quenching of the high enthalpy source water by cold meteoric dilution water preserves a low pH accompanying the temperature drop, in part because CO₂ losses are minimized, and because oxidation of dissolved sulfide by dissolved oxygen in the meteoric water releases H⁺ ions. Conductive cooling requires ample contact opportunity between the fluid and wall rocks (TRUEDELLE *et al.*, 1977), hence dissolved CO₂ is more likely to react with Na-silicates yielding Na⁺ and HCO₃⁻ ions (FOURNIER and TRUEDELLE, 1970), and dissolved sulfide may be lost to form pyrite (ELLIS, 1973; WEISSBERG, 1969).

During final fluid ascent to the surface important reactions involving As and Sb might potentially include: redox reactions, halogen complexation with gas-phase partitioning, sulfide precipitation, hydrolysis of As (III) and Sb(III), and in the oxidized epithermal zone, interactions of As(V) with Fe. Based on ΔG , data (WAGMAN *et al.*, 1968), complexation by halogens is highly unfavorable at the neutral-alkaline pH's and dropping temperatures enroute from the intermediate enthalpy reservoir(s). Stibnite (Sb₂S₃), orpiment (As₂S₃) realgar (AsS), and arsenopyrite (FeAsS) are the likely mineral phases controlling Sb and As under reducing conditions (WHITE, 1967; WEISSBERG, 1969). Unfortunately, because of gaps in the essential thermodynamic data (especially at elevated temperature), a complete chemical equilibrium model cannot be specified as yet for either As(III) or Sb(III) in geothermal waters. The thermodynamic data suggest, however, that arsenic should be more soluble than antimony in these waters, and that because of hydroxyl and bisulfide complexing, solubilities should increase sharply with increasing temperature and pH (*cf.* WEISSBERG *et al.*, 1966; MESMER and BAES, 1976).

RESULTS

Stability in arsenic concentration over time: same source

The arsenic concentrations and Cl/As ratios are remarkably constant over time spans of a few weeks to a few years (Table 1). Among the bicarbonate-buffered springs, the variation in Cl/As is greatest for Cistern, a diluted spring in the Norris Basin known for its highly erratic Cl concentration. If we exclude the untreated Mammoth samples (with their very high and unstable Ca concentrations), the As contents of the travertine-depositing springs are also notably time stable. In addition to specific spring contrasts, two samples taken ~13 days apart from the lower Firehole River during an autumnal (1974) base-flow period had Cl concentrations of 54 and 56 mg L⁻¹, and identical total As concentrations (0.252 mg L⁻¹).

Table 1. Arsenic contents of Yellowstone hot springs sampled on more than one occasion.

Location	Sample I.D., Treatment*, and Date	Cl As		Cl/As Atoms	c.v. As
		(mg L ⁻¹)			
Upper Basin					
Old Faithful Seep	YF-492, RU, 5/70	362	1.275	599	
	YS-74-122, FA, 9/74	365	1.275	604	0.8%
	YJ-74-19, FU, 10/74	373	1.260	627	
Ear	YT-73-71, FA, 9/73	403	1.355	629	
	YJ-74-11, RU, 10/74	414	1.370	639	0.8%
Tortoise Shell	YS-74-123, FA, 9/74	389	1.620	507	
	YJ-74-6, RU, 10/74	378	1.580	506	1.9%
Witches Cauldron	YS-74-125, FA, 9/74	377	1.500	532	
	YJ-75-10, RU, 10/74	349	1.510	489	0.5%
Interchange	YS-74-128, FA, 9/74	242	0.895	571	
	YJ-74-17, RU, 10/74	226	0.920	519	2.0%
Lower Basin					
Octopus	YS-74-112, FA, 9/74	263	1.455	382	
	YJ-74-51, RU, 10/74	255	1.465	368	0.3%
Azure Pool	YS-74-132, FA, 9/74	318	1.480	455	
	YT-74-2, RU, 7/74	---	1.445	---	1.7%
Ojo Caliente	YF-351, RU, 6/67	331	1.520	459	
	YJ-75-60, FU, 6/75	318	1.435	468	4.1%
Snort	YF-353, RU, 6/67	344	1.725	420	
	YJ-75-11, FU, 6/75	331	1.640	427	3.7%
Gibbon-Norris Basins					
Sylvan	YT-73-82, RU, 9/73	531	2.935	382	
	YJ-74-21, FU, 10/74	551	3.000	388	1.6%
Pork Chop	YF-498, RU, 6/71	782	2.855	579	
	YF-557, RU, 9/72	780	2.975	554	
	YJ-75-34, FU, 6/75	712	2.755	546	3.8%
Base Porcelain Terrace	YF-360, RU, 7/67	706	2.815	529	
	YF-554, RU, 9/72	709	2.955	507	
	YT-73-74, FA, 10/73	704	2.810	529	4.2%
Perpetual Spouter	YJ-75-28, FU, 6/75	664	2.665	526	
	YF-499, RU, 6/71	593	2.270	552	
	YF-556, RU, 9/72	558	2.100	561	4.1%
Cistern	YJ-75-33, FU, 6/75	557	2.235	526	
	YF-361, RU, 7/67	476	1.540	652	
	YF-558, RU, 9/73	464	1.710	574	
Little Whirligig	YT-74-45, RU, 7/74	462	1.435	680	22.2%
	YJ-75-32, FU, 6/75	293	0.975	634	
	YF-555, RU, 9/72	582	3.300	373	5.5%
Echinus	YT-73-61, FA, 9/73	587	3.565	348	
	YF-497, RU, 6/71	112	0.160	1470	2.2%
Fenner Drill Hole	YJ-75-35, FU, 6/75	110	0.165	1320	
	YT-74-46, RU, 7/74	---	2.285	---	1.0%
Mammoth	YJ-75-27, FU, 6/75	664	2.315	606	
	YF-567, RU, 9/72	162	0.630	543	
	YJ-73-1, FA, 9/73	168	0.605	585	6.1%
Blue	YS-74-147, FA, 9/74	166	0.685	514	
	YF-569, RU, 9/72	171	0.355	1010	
	YT-73-65, FA, 9/73	166	0.620	566	32%
New Highland	YS-74-146, FA, 9/74	171	0.690	524	
	YF-570, RU, 9/72	154	0.240	1350	48%
Elephant Back	YJ-73-3, FA, 9/73	157	0.490	680	
	YF-570, RU, 9/72	154	0.240	1350	48%
Miscellaneous					
Terrace	YF-529, RU, 5/72	65	0.190	715	
	YJ-73-16, RU, 9/73	65	0.170	818	9.4%
Calcite	YT-69-1A, FA, 7/69	---	1.385	---	
	YS-74-144, FA, 9/74	242	1.450	358	3.3%

* Sample treatments: FA - filtered (0.1 or 0.45 μ m) and acidified while hot in the field, FU - filtered, unacidified in field. RU - untreated (raw sample).

These samples are evidence of a nearly constant spatially integrated flux of As (as well as Cl) from the combined Lower-Midway-Upper Basin thermal region (FOURNIER *et al.*, 1976; STAUFFER *et al.*, 1980).

Comparisons with earlier As data sets for the Park (*cf.* ROWE *et al.*, 1973) are less definitive, because of probable analytical errors in some of the earlier data, and the nonavailability of these earlier samples for reanalysis. Thus, GOOCH and WHITFIELD (1888) reported As = 1.6 mg L⁻¹ (Cl/As = 579) for Old Faithful Geyser, but only 0.45 mg L⁻¹ (Cl/As = 2065) for

closely neighboring Giantess Geyser (both sampled August 1884). Similarly, the reported (sampled 9/59) As concentration for Occasional Geyser (West Thumb Basin; As < 0.01; Cl/As > 10,000) is incompatible with that for closely neighboring Abyss Pool (sampled 9/60; As = 2.0; Cl/As = 314). The earlier result for Abyss Pool is indistinguishable from our extensive survey of West Thumb in 1974.

A statistical comparison of the data compiled by ROWE *et al.* (1973), Noguchi's data from 1971 (*cf.* BROCK, 1978), and results of this study reveals no time trends in As or Cl/As (Tables 1, 2; Fig. 2). Thus, Excelsior Crater in Midway Basin was first sampled and analyzed in 1884, and resampled and analyzed in 1959, 1960, 1971 (Noguchi), and 1973 (our work), always with the same result. The area near Great Fountain Geyser was very rich in As in both 1960 and 1974, whereas Black Warrior Lake had undetectable As in 1959, 1961, and again in 1974. Much like its Cl, B, Li, HCO₃, F, Ca, Na, K, and SiO₂ content, the As concentration of a YNP hot spring or geyser is part of an enduring (our lifespan) chemical fingerprint.

Arsenic vs. chloride diagrams

ELLIS (1973) and MAHON (1970) noted that elevated As concentrations occur only in those geothermal waters which are also enriched in Cl (relative to the cold source water in the convecting system). The same pattern is observed in Yellowstone, where dilute warm springs in Gibbon Meadows (Cl = 7 and 1 mg L⁻¹) and Black Sand Basin (Cl = 4 mg L⁻¹) have As < 0.015 mg L⁻¹. The same is true of the two boiling Washburn Springs (Cl = 7 and 2 mg L⁻¹) and a condensed vapor sample collected over a fumarole in the White Creek area of Lower Geyser Basin.

Table 2. Inter-laboratory comparison of arsenic concentrations for named springs south of Madison Junction, YNP.

Spring Name	Stauffer		Noguchi		ΔAs †
	As	Cl/As	As	Cl/As	
West Thumb Basin					
Ephedra	2.000 ^C	318	2.06	293	-0.06
Twin Geyser	1.955 ^C	311	1.89	322	+0.06
Upper Basin					
Old Faithful	1.650 ^D	615	1.60	597	+0.05
Chinaman	1.275 ^C	624	1.41	579	-0.14
Three Sisters	1.430 ^C	590	1.20	728	+0.23
Tortoise Shell	1.620 ^C	507	1.78	463	-0.16
Ink Well	1.210 ^C	460	1.19	475	+0.02
Morning Glory	1.310 ^C	470	1.36	459	-0.05
Mirror Pool	1.395 ^C	417	1.21	500	+0.19
Middle-Lower Basins					
Excelsior Crater	1.945 ^B	289	2.02*	303*	-0.08
Octopus	1.460 ^C	375	1.28	422	+0.18
Ojo Caliente	1.435 ^A	468	1.41	486	+0.03
Boulder	1.530 ^D	412	1.47	439	+0.06
Spray Geyser	0.735 ^D	528	0.78	514	-0.04
Imperial Geyser	0.835 ^D	509	0.92	470	-0.08
Red Terrace	1.100 ^D	492	0.89	624	+0.21
Queens Laundry	1.005 ^D	474	0.89	562	+0.12
Steep Cone	1.095 ^D	493	0.92	596	+0.18

Years sampled: A - 1967 (Fournier); B - 1973 (Truesdell); C - 1974 (the authors); D - 1975 (Thompson). All Noguchi samples collected in summer 1971 and analyzed in Japan.

*Mean values for four separate crater samples.
 †Difference between paired results for Stauffer vs. Noguchi. The mean difference for the 18 pairs is +0.04 (not significantly different than zero).

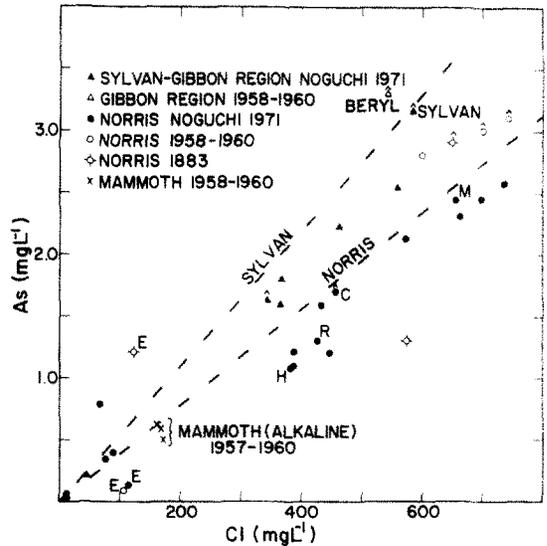


FIG. 2. Arsenic vs. chloride concentrations for earlier sample surveys (antedating this work) north of Madison Junction. Spring names: E = Echinus; H = Horseshoe; R = Realgar; C = Cistern; M = Emerald. Note: Bicarbonate-buffered springs have ⁻ above symbol.

The differential effects of cooling pathways as As are revealed using As vs. Cl diagrams. Figure 3 illustrates the procedure as applied to the Upper Geyser Basin. Here, the positions of "points" corresponding to individual spring samples are examined relative to the "radial line" connecting key indicator spring point(s) and the graph origin.

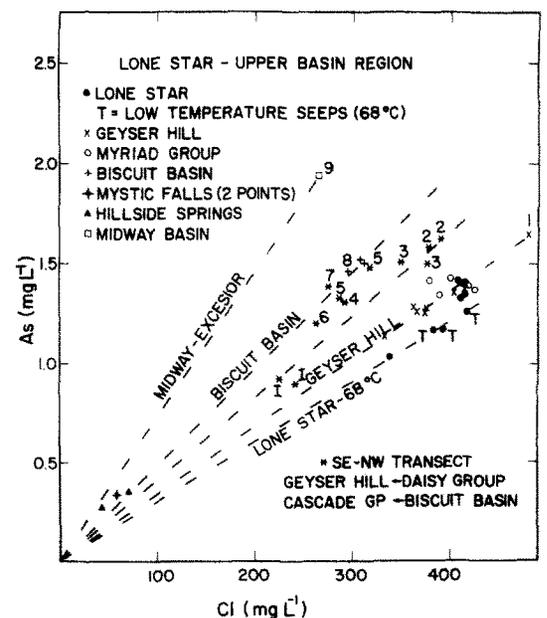


FIG. 3. Arsenic vs. chloride concentrations for the Lone Star-Upper-Biscuit Basin region. Spring names along the SE-NW transect are: #1 = Old Faithful Geyser; #2 = Tortoise Shell; #3 = Witches Cauldron; #4 = Morning Glory; #5 = Spouter; #6 = Inkwell; #8 = Sapphire Geyser; #9 = Excelsior Crater. I = Interchange Spring.

hot water interactions with bay sediments along the upflow zone extending under the bay. West Thumb Bay occupies a mini caldera set within the larger Yellowstone caldera (CHRISTIANSEN and BLANK, 1972), and is widely underlain by hot water (MORGAN *et al.*, 1976).

Closely neighboring Potts Basin is another geographically confined set of springs with narrowly ranging geochemical ratios (Table 3). No spring has an indicated As loss > 10%. A warm spring (68°C) with Cl = 48 mg L⁻¹ experienced a loss of 7% of its original As. Arsenic losses accompanying dilution are also minor at Heart Lake (<17%, Fig. 4).

The potential effects of large scale dilution by meteoric water on As are well illustrated in the White Creek-Black Warrior-Fountain region of Lower Geyser Basin (Fig. 6). Based on the Cl/B and Cl/Li ratios, a common high-Cl source water may feed this area. However, As is nearly absent from most of the spring waters with Cl < 70 mg L⁻¹. Only two of 11 samples in this class have Cl/As < 2500. The high Cl/As ratios are associated with low Cl, low field pH, low Cl/SO₄, and high Ca, Mg, and Mn concentrations (Table 4). The one sample with both low Cl (57 mg L⁻¹) and low Cl/As (285) has much reduced Ca, Mn, and SO₄ concentrations as compared to the other low-Cl springs, and is located near the boundary between the low and high Cl waters in the White Creek area.

Table 3. Compilation of geochemical ratios for geothermal regions of YNP.

Location - n; No. of Samples	Mean ratios and coefficient variation (%)*				
	Cl/As	Cl/B	Cl/F	Cl/Li	Cl/EO ₃
South Park Region					
Shoshone - 29	596(16)	24.4(12)	5.1(16)	30(57)	0.8(45)
Heart Lake - 9	555(6)	27.2(6)	6.2(11)	12.8(9)	1.7(12)
West Thumb - 23	327(4)	27.1(7)	9.8(15)	18.8(22)	0.93(14)
Potts - 10	291(4)	29.6(5)	4.8	12.0(10)	0.91(8)
Lone Star-Upper Basin					
Lone Star - 8	657(6)	27.7(2)	12.8(13)	38.0(26)	5.0(40)
Geyser Hill - 7	624(2)	31.3(14)	9.1(15)	15.3(9)	3.9(13)
Myriad - 5	611(6)	30.3(4)	8.5(7)	15.7(6)	2.8(46)
Cascade - 7	443(4)	28.3(10)	5.6(4)	15.8(8)	0.88(5)
Biscuit - 2	432(1)	31.0(2)	5.3(2)	27.6(1)	0.91(1)
Black Sand - 3	447(2)	30.9	5.9(3)	18.4(5)	0.88(4)
Hillside - 6	410(8)	21.1(9)	3.1(10)	18.9(6)	0.45(18)
Mystic Falls - 2	389(2)	20.5(3)	---	22.7(3)	0.43(12)
Midway-Lower Basins					
Flood - 4	333(11)	30.2(3)	6.4(5)	13.4(10)	0.95(8)
Rabbit - 14	362(6)	30.6(6)	6.1(3)	12.8(13)	1.16(15)
Excelsior - 1	266	28.8 [†]	6.8 [†]	20.0 [†]	0.86 [†]
Lower White* - 4	301(26)	29.8(3)	6.9(15)	17.4(16)	1.37(9)
Firehole Lake - 7	~6000	28.1(8)	2.7(30)	20.5(20)	0.49(24)
Fountain - 2	263(2)	27.1	7.5(8)	23.8(7)	1.5(27)
Nex Perce - 4	456(8)	25.2(8)	5.5(4)	16.3(9)	2.5(32)
River - 15	446(11)	27.4(5)	5.4(4)	25.9(21)	2.4(17)
Fairy - 1	412	24.0	5.2	18.4	2.1
Imperial-Spray - 2	519(3)	26.5(17)	---	16.4(1)	0.83(1)
Sentinel Meadow - 4	490(2)	23.3(14)	5.0(2)	27.1(20)	1.3(15)
North of Madison Junction					
Terrace Spring - 2	770(10)	18.1(9)	5.6(11)	19.5(10)	0.14(2)
Beryl Spring - 1	345 [†]	21.1 [†]	18.1 [†]	17.4 [†]	7.2 [†]
Artist Paint P. - 3	423(4)	22.5(4)	18.5(5)	16.4(4)	6.8(19)
Sylvan Area - 3	379(3)	17.5(2)	15.6(5)	19.2(13)	N.A.
Norris - 21 [‡]	559(17)	20.0(6)	56.0(18)	23.8(10)	N.A.
Mammoth - 5 [§]	574(11)	13.3(2)	36.0(10)	20.3(2)	0.33(11)
Yellowstone Canyon					
Seven Mile Hole - 1	669	9.5	17.0	23.7	3.1
Calcite Spring - 1	358	---	30.0	21.2	1.6
Joseph's Coat - 1	90	9.3	37.0	20.7	11.8

*Atomic ratios except for Cl/EO₃ (equivalence); to obtain c.v. for the mean multiply by n^{1/2}.

[†]Based on earlier spring samples reported in Rowe *et al.* (1973).

[‡]Four samples with Cl > 150 in vicinity of Great Fountain Geyser and including "Five Sisters" and "Octopus" springs.

[§]Three highly acidic Norris samples with dilute Cl excluded.

[§]Field-acidified samples only.

Other more isolated examples of apparent As losses accompanying dilution include Interchange Spring in Upper Geyser Basin (Fig. 3) and Terrace Spring (Cl = 65 mg L⁻¹) near Madison Junction (*cf.* FOURNIER and TRUESDELL, 1974). The Cl/As ratio at Terrace Spring ranges from 715 to 820, e.g. more than double the ratio of Beryl Spring (345) in the same general region.

A dilute Cl level does not *imply* As losses from solution, however. In addition to the examples cited from Potts, West Thumb, and White Creek, all of the sampled springs in the Hillside and Mystic Falls regions of Upper Basin have low Cl/As ratios. These sources have large flows, and relatively high SiO₂ for their Cl concentrations (FOURNIER *et al.*, 1976). In the Yellowstone Canyon region, boiling Calcite Spring and two adjacent warm springs with highly diluted Cl have nearly identical Cl/As (Fig. 7).

Effects of dilution north of Madison Junction. The Norris area differs from areas previously discussed in that the high-Cl As-bearing parent is weakly bicarbonate buffered, hence significant upper zone dilution by acid-sulfate water frequently results in low pH mixture (WHITE *et al.*, 1971; TRUESDELL and FOURNIER, 1976). The Norris waters are thus conveniently classified as follows: 1) weakly bicarbonate buffered with intermediate to high Cl concentrations (450 to 780 mg L⁻¹) and low SO₄; 2) weakly acidic (pH = 4 to 6) with intermediate Cl and moderate SO₄; 3) highly acidic (pH < 4) low-Cl-high-SO₄ waters.

Based on seven separate samples collected over an eight year time span from "Pork Chop" and Base of Porcelain Terrace, the Cl/As ratio for the undiluted bicarbonate-buffered Norris deep water is 539 ± 9. This ratio defines the Norris radial line in Figs. 2 and 7. The three samples from alkaline "Spouter" fall on the radial line (mean Cl/As = 546 ± 11). By contrast, the moderately *acidic* Fenner Drill Hole Spring sample plots significantly below the radial line (by 11%) despite its higher Cl concentration.

Among the more dilute Norris springs the As losses are modest unless the water is acidic (average loss at Cistern is only 14%). Six Norris samples have Cl/As > 690; three ratios > 1000. Two of the latter samples had low field pH's (2.8 and 3.3). A field pH was not determined on the third sample (YF-497), however, the low Cl (112 mg L⁻¹) and high SO₄ (283 mg L⁻¹) assure that the spring water was initially highly acidic. Little Whirligig is unique among the Norris springs studied in that it consistently combines a low Cl/As with a moderately acidic pH.

Geographic variations in As in YNP

Examining the radial lines in Figs. 3, 4, 6 and 7, the Cl/As ratio is not constant in the Park. Instead, loci rich in As (low ratios) exist in the Potts-West Thumb region, the NW section of Upper Geyser Basin, Midway Basin, the lower White Creek and Fountain regions of Lower Basin, Gibbon Basin, Calcite Spring and Joseph's Coat Spring (Mirror

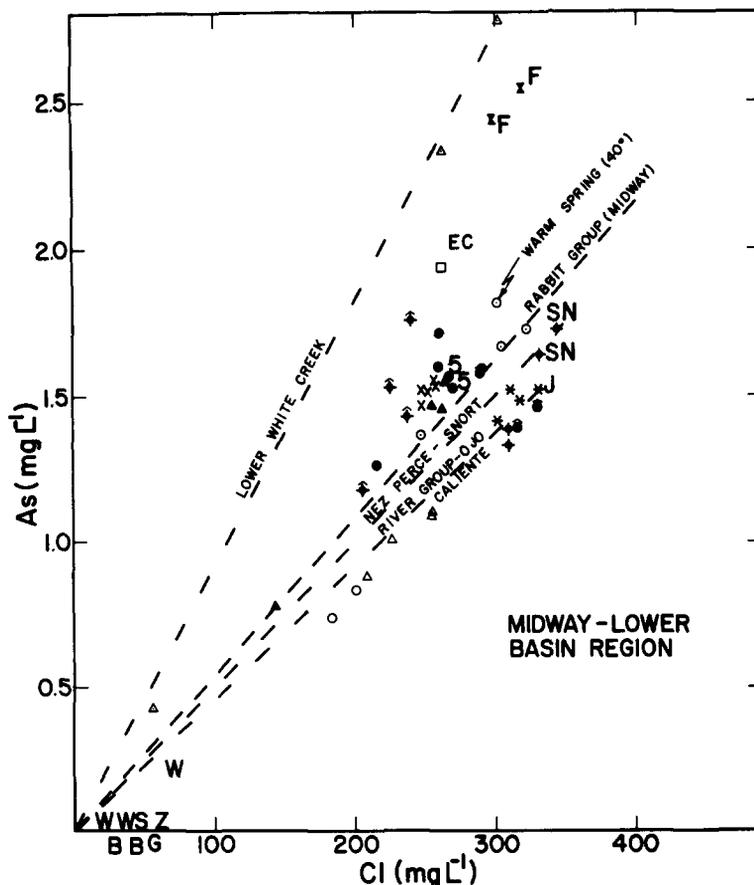


FIG. 6. Arsenic vs. chloride concentrations for the Midway-Lower Geyser Basins. Symbols: \diamond , Flood Group (Midway); \bullet , Lower Rabbit (Midway) (the superscript "5" denotes two samples from spring adjacent to Y-5 drill hole); \circ , Upper Rabbit (Midway); \square , Excelsior Crater (Midway); Δ , Middle White Creek (vicinity of Octopus Spring); \blacktriangle , Lower White Creek, W = dilute springs in Upper White Creek region; B = Black Warrior; Z = Zomar; S = Steady Geyser; G = Grey-Bulger; \blacklozenge , Nez Perce Group (SN denotes Snort Spring); \circ , Imperial and Spray Geysers; Δ , River Group (J = Ojo Caliente).

Plateau). However, the geographically dispersed Mammoth, Norris, Shoshone, and Heart Lake thermal basins have key indicator Cl/As ranging only from

533 to 565. Significantly higher ratios occur at Lone Star (616), Geyser Hill (615), and at Seven Mile Hole Spring (669).

Table 4. Chemical compositions of thermal springs proceeding downgradient along the White Creek sampling transect: Lower Geyser Basin 1974.*

Sample No.	44	45	46	47	48	49	50 [†]	51 [‡]	52 [§]
Temperature	73	71	85	74	61	93	85	70	75
pH (field)	5.0	5.9	--	6.5	4.8	7.1	8.5	7.5	7.0
Cl	19	34	70	50	18	143	265	255	304
SiO ₂	137	159	183	169	158	223	272	270	298
SO ₄	23	23	21	24	20	18	19	18	19
Ca	14.2	11.8	11.2	13.4	14.5	5.2	0.3	0.2	0.1
Mg	0.40	0.42	0.21	0.26	0.39	0.01	<0.01	<0.01	<0.01
Mn	0.47	0.09	0.14	0.07	0.10	0.07	<0.02	<0.02	<0.02
Cl/B	29.**	26.**	27.**	30.**	55.**	27.3	29.9	28.8	30.7
Cl/CO ₃	0.28	0.43	0.70	0.59	0.26	0.91	1.26	1.27	1.40
Cl/F	1.5	2.2	3.7	3.1	1.4	5.6	6.2	5.9	7.4
Cl/Li	14.2	25.8	19.0	32.6	13.6	16.5	15.3	16.1	16.5
Cl/As	>2600	>10,000	672	>5000	>2500	398	361	382	231

* All concentrations mg L⁻¹; atomic ratios. Sample #44 is "source B"; #45 is "source A" for White Creek. Note: #46, 47, 49 are "transitional" in type.
[†]Five Sisters Spring.
[‡]Octopus Spring.
[§]Unnamed near Firehole Loop Road and "White Dome Geyser".
^{**}Cl/B ratios have high uncertainty because of low B concentrations.
^{||}Equivalence ratios.

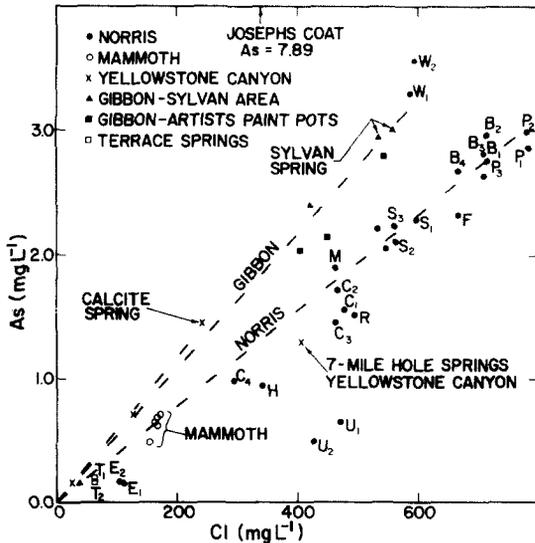


FIG. 7. Arsenic vs. chloride for thermal waters north of Madison Junction and in the Yellowstone Canyon Region. Spring names: B = Base Porcelain Terrace; C = Cistern; E = Echinus; F = Fenner Drillhole Spring; H = Horseshoe; M = Emerald; P = Pork Chop; R = Realgar; S = Spouter; T = Terrace; U = unnamed acidic springs collected by R. O. Fournier; W = Little Whirligig. Subscripted numbers denote chronological order (1 is earliest) for springs with multiple samples (see Table 1).

Because of the large number of spring samples, the high analytical precision, and the stability of spring composition over time, we also conclude that certain spring groups in close geographic proximity have significantly different Cl/As indicator ratios. For example, Potts has significantly more As than West Thumb, and Sylvan has more than Artist's Paint Pots.

Within the geographically extensive Upper-Midway region, the Cl/As ratio drops systematically as one proceeds NW along the transect from Geyser Hill to Biscuit Basin and then on to Midway (Table 3). The Myriad and Geyser Hill Groups have statistically equivalent Cl/As ratios which also agree with the best indicators from Lone Star Basin further to the SE. Transitional springs positioned between Geyser Hill and the Cascade Group have intermediate Cl/As ratios. Along the parallel transect connecting Black Sand Basin with Mystic Falls, the Cl/As ratio drops from 447 to 389.

Geochemical correlates of Cl/As: YNP

Geographic variations in the Cl/As ratio are generally unrelated to geographic contrasts in the Cl/F, Cl/B, and Cl/Li ratios (Table 3). No general relationship between Cl/As and Cl/F was expected because fluorite (CaF_2) partially controls F in geothermal waters (ELLIS, 1967, 1973; STAUFFER, 1982), and unlike As and Cl, F^- is non-negligible in cold spring waters of YNP (sometimes $>1.5 \text{ mg L}^{-1}$). Fluorite equilibria probably account for the low F and high Cl/F ratios north of Madison Junction (STAUFFER,

1982). However, the Cl/As ratio is generally unrelated to this major shift in Cl/F (Table 3). Except in the Lone Star-Upper Basin complex, the two ratios are also unrelated in more localized comparisons (Table 3).

Comparisons between Cl/As and Cl/B are useful because boron acts conservatively once in solution. The Cl/B ratios are lower and more variable north of Madison Junction, probably because of hot water leaching of sedimentary formations. Particularly low Cl/B ratios are observed in the Yellowstone Canyon and Mammoth areas. South of Madison Junction low Cl/B ratios occur at Mystic Falls and Hillside. The Heart Lake, West Thumb, Potts, Lone Star, Upper, Midway, and SE Lower Basins all have statistically equivalent Cl/B ratios; these geographic areas have Cl/As indicator ratios ranging from ~ 250 to 616.

If As, Cl, and Li were all derived from a common deep enthalpy reservoir, and all behaved conservatively during fluid migration, then the Cl/Li and Cl/As ratios would be closely correlated in the park. Instead, they are not (Table 3). Low Cl/Li ratios at Midway, Heart Lake and Potts Geyser Basins are associated with both low and moderately high Cl/As ratios. Conversely, relatively high Cl/Li ratios at Biscuit Basin, Shoshone, Lone Star, Lower Geyser Basins, and the Yellowstone Canyon areas are associated with both high and low Cl/As ratios. A wide range in Cl/As ratios is also observed for spring groups with intermediate Cl/Li ratios (contrast Geyser Hill with the Cascade and Black Sand Basin waters). Because of the relatively strong correlation between Li and Cs for the Park waters (R. E. STAUFFER, unpubl.), one can also infer that the geographic differences in the Cl/As ratio are also unrelated to changes in the Cl/Cs ratio.

Low Cl/As ratios are associated with low $\text{Cl}/\Sigma\text{CO}_3$ ratios, provided that Cl levels exceed $\sim 200 \text{ mg L}^{-1}$ (Table 3, Fig. 8). The West Thumb, Potts, Midway, Lower White Creek, Fountain, Black Sand, Biscuit, and Cascade areas (the last three within Upper Basin) all have relatively low Cl/As and $\text{Cl}/\Sigma\text{CO}_3$ ratios. Conversely, the Lone Star, Myriad, Geyser Hill, and Norris areas all have high-Cl waters with high Cl/As and $\text{Cl}/\Sigma\text{CO}_3$ ratios. Within the Yellowstone Canyon, Seven Mile Hole spring has high ratios; Calcite Spring has low ratios. In the Gibbon Basin and at Joseph's Coat Spring low Cl/As ratios are associated with high $\text{Cl}/\Sigma\text{CO}_3$ ratios. Although the high-Cl thermal waters are weakly buffered by bicarbonate at the surface, these same spring waters also have highly elevated SO_4 concentrations (typically 150 to 350 mg L^{-1}) and alkalinity has been lost by reaction with sulfuric acid (*cf.* TRUESDELL *et al.*, 1978).

The regional correlation between Cl/As and $\text{Cl}/\Sigma\text{CO}_3$ is best illustrated by the extensively sampled Upper Basin complex, extended to include Lone Star and Biscuit Basins (Figs. 9, 10). Trends in both geochemical ratios are oriented along the SE-NW

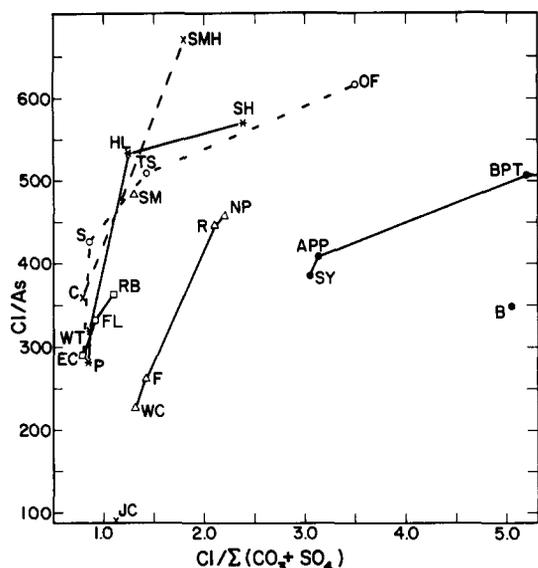


FIG. 8. Cl/As vs. Cl/Σ(CO₃ + SO₄) for YNP thermal regions. Spring names: [BPT = Base Porcelain Terrace, APP = Artists Paint Pots, Sy = Sylvan; B = Beryl]; [NP = Nez Perce; R = River Group; F = Fountain, WC = Lower White Creek]; [Rb = Rabbit Group; Fl = Flood Group; EC = Excelsior Crater]; [OF = Old Faithful Geyser; TS = Tortoise Shell; S = Sapphire Geyser (Biscuit Basin); EC = Excelsior crater]; [SMH = Seven Mile Hole; C = Calcite Spring]; [SH = Shoshone; HL = Heart Lake; WT = West Thumb; P = Potts]; JC = Joseph's Coat.

axis of thermal activity. The arsenic and alkalinity compositions of geographically transitional springs such as Tortoise Shell, Witches Cauldron, and Morning Glory Pool are clearly transitional between Geyser Hill type water and the high alkalinity-high arsenic waters of Biscuit Basin. A two-source mixing model can account for the range in Cl/As and ClΣCO₃. However, both Lone Star and Biscuit Basin have

incompatibly high Cl/Li ratios, and Hillside-Mystic Falls has too low a Cl/B ratio (Table 3) to accept such a simple source mixing model.

Elsewhere, within the geographically confined Shoshone, Heart Lake, West Thumb, and Midway basins, we can still detect a positive correlation between the *intra*-basin Cl/As ratios and Cl/ΣCO₃ ratios (Figs. 11–13).

The hot spring basins with the highest regional Cl levels and hottest indicated reservoir temperatures (silica geothermometer) have the highest Cl/As indicator ratios (hence are poorest in As per unit Cl) in Yellowstone Park (Fig. 14). Thus, Geyser Hill has the highest ratio south of Madison Junction; and Norris is much poorer in As than Gibbon and Beryl Spring. In the Yellowstone Canyon region the high-Cl Seven Mile Hole sample has 55% as much As (per unit Cl) as Calcite Spring, and only 13% of the As in Joseph's Coat Spring. Paradoxically, the three Park samples which would have had both the least opportunity and least propensity to precipitate As among all the springs sampled (Old Faithful, Base Porcelain Terrace, Pork Chop) are relatively impoverished in As as compared to the Park norm. However, these same samples are not impoverished relative to their own spring group!

Antimony in Yellowstone Park Geothermal Waters

Based on much sparser data of poorer precision (Table 5), the geochemistry of Sb does not closely parallel As in the hot-spring waters. In the Upper Geyser Basin both the Cl/Sb and As/Sb ratios *increase* dramatically as one proceeds NW from Geyser Hill to the Biscuit Basin. Because the Cl/As ratio decreases along the transect, the As/Sb ratio at Sapphire Geyser is 3.4 times greater than at the Seep spring on Old Faithful mound. Because Ear Spring (Geyser Hill)

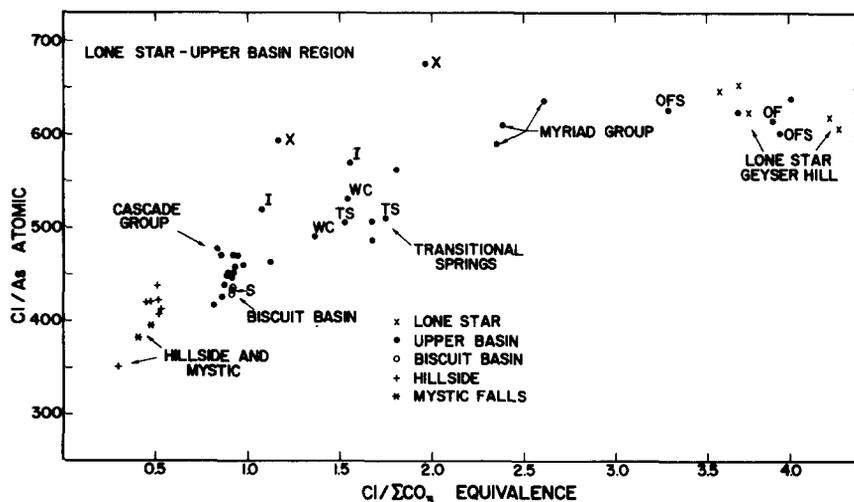


FIG. 9. Cl/As vs. Cl/ΣCO₃ for Lone Star-Upper Basin Region. Spring names: OF = Old Faithful Geyser; OFS = Old Faithful Seep; TS = Tortoise Shell; WC = Witches Cauldron; I = Interchange; S = Sapphire. Two springs marked by × exhibit chemical anomalies (the Cl/ΣCO₃ ratio may be in error).

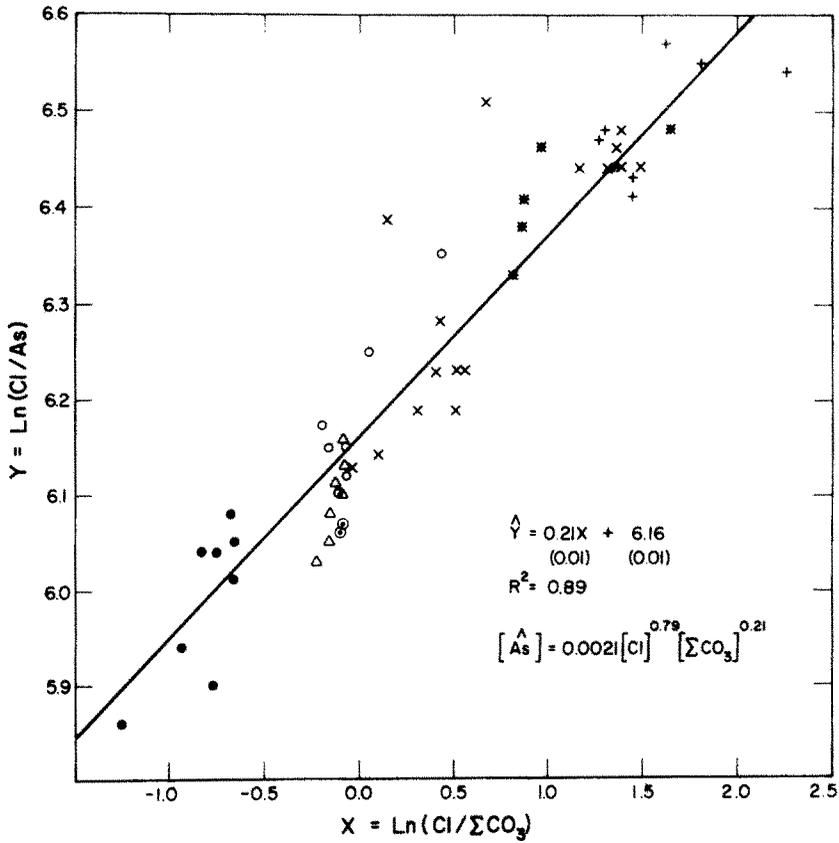


FIG. 10. Log-linear transformation of Cl/As vs. Cl/ΣCO₃ for Upper Basin region.

has considerably higher Cl/Sb and As/Sb ratios than the Seep, but otherwise similar basic chemistry, the decrease in Sb along the SE-NW transect of upper basin cannot be exclusively the result of different Cl/Sb ratios in the parent enthalpy reservoirs.

Upper zone mixing with meteoric water results in Sb losses, the effect being more extreme than for As. In West Thumb Basin the two analyzed representatives of the reduced Cl class have higher Cl/Sb and

As/Sb ratios than the high-Cl class. Similarly, Octopus Spring, in the White Creek area, has the highest Cl/Sb ratio among the six Midway-Lower Basin samples. Azure Pool and Ojo Caliente in the River Group have relatively high Cl concentrations (for the Lower Basin), high Cl/ΣCO₃ ratios and low Cl/Sb and As/Sb ratios.

North of Madison Junction, the two Norris samples are impoverished in Sb, thus leading to very high As/

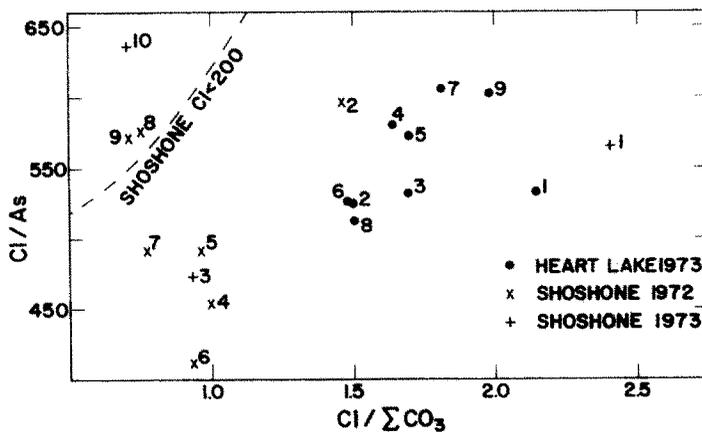
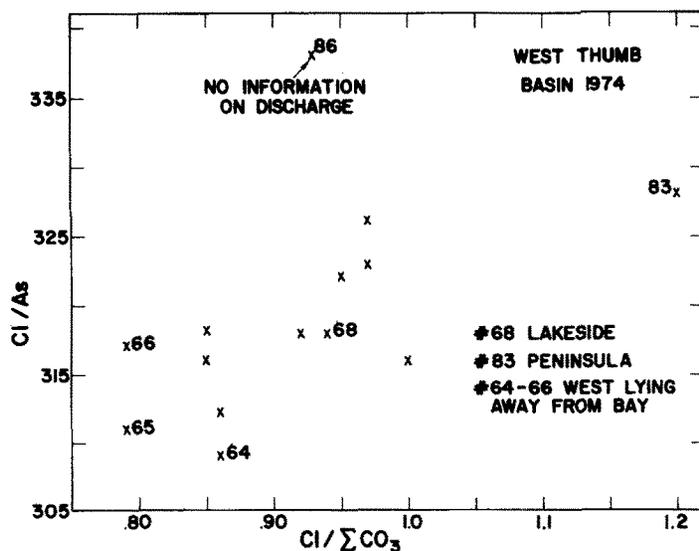


FIG. 11. Cl/As vs. Cl/ΣCO₃ for Shoshone and Heart Lake Basins. The springs are numbered in descending order of Cl concentrations.

FIG. 12. Cl/As vs. Cl/ΣCO₃ for West Thumb Geysers Basin.

Sb ratios. The lone Mammoth sample features the lowest Sb concentration and the highest Cl/Sb and As/Sb ratios among the samples. Mammoth Hot Springs is also characterized by significant ($\sim 3 \text{ mg L}^{-1}$) dissolved sulfide (THOMPSON *et al.*, 1975), low sub-surface pH and sub-boiling temperatures. Calcite Springs has more Sb than Mammoth despite geochemical similarities between the two areas.

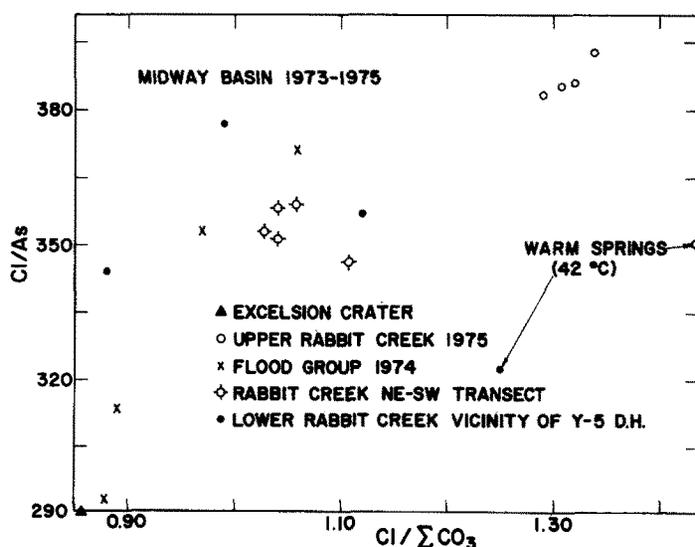
DISCUSSION

Predictive capabilities of chemical models

Thermodynamic data indicate gas-phase partitioning of As and Sb is unlikely to be important accompanying adiabatic cooling below $\sim 200^\circ\text{C}$. This prediction is borne out by the near absence of As in springs heated by condensing vapors.

The partial precipitation of As and Sb following mixing of a high temperature, high Cl, As-Sb bearing parent water with cold meteoric water is also in qualitative agreement with thermodynamic models. In general, low temperatures and pH's following dilution favor sulfide deposition, provided Eh also remains low. These special conditions are best satisfied at Norris where mixing involves an acid-sulfate component and a poorly buffered Cl-As rich parent. Thus, WEED and PIRSSON (1891) reported orpiment and realgar deposition in sinter cavities beneath the lip of an acidic clearwater spring in Norris.

Furthermore, temporal shifts in the As(III):H⁺:H₂S:temperature domain could easily shift the sulfide saturation indices and initiate reworking of previously deposited minerals. This might explain the relatively high As concentrations in Little Whirligig

FIG. 13. Cl/As vs. Cl/ΣCO₃ for Midway Basin.

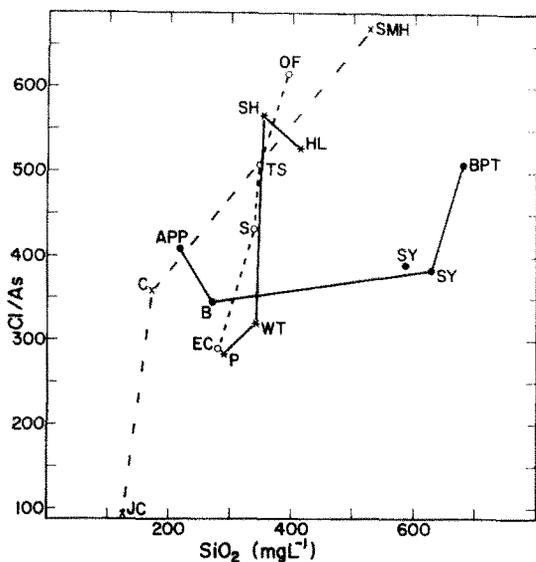


FIG. 14. Cl/As vs. SiO₂ by region. See Fig. 8 for letter designations.

(Norris). The very high As concentration and low Cl/As (90) at Joseph's Coat Spring in 1974 may also result from As remobilization following an influx of alkaline Cl-rich water. Previously, this area had been known for its arsenical deposits accompanying acid conditions (HAGUE, 1887; THOMPSON *et al.*, 1975).

Elsewhere in the Park, where alkalinity is retained following mixing, arsenic losses following mixing are usually minor for discharging springs unless the final Cl concentration is below 100 mg L⁻¹, and there is evidence of an upward redox shift and subsequent Fe deposition in the subsurface. The arsenic losses probably occur following dilution and oxidation (by O₂) of As(III) and Fe(II). Thus, STAUFFER *et al.* (1980) reported dissolved oxygen (0.9 mg L⁻¹) in the upwelling waters of Octopus Spring, and showed that the As in both the spring and the adjacent White Creek is almost entirely As(V). The correlation between As losses and Mn concentrations in the White Creek area may be due to the higher mobility of Mn at the transitional redox values where Fe is oxidized. A sample from Steady Geyser collected by Alfred Truesdell in 1969 had total Al, Fe, and Mn concentrations (0.15, 0.11, 0.15 mg L⁻¹; THOMPSON *et al.*, 1975) one-two orders of magnitude higher than the typical alkaline boiling hot spring water with high Cl in Yellowstone Park (STAUFFER *et al.*, 1980). High concentrations of Mn persisted in a filtered 1973 Steady Geyser sample (STAUFFER *et al.*, 1980). The mildly acidic pH's in the Upper White Creek springs are highly favorable for adsorption losses of As(V) on hydrous ferric oxides (PORTMANN and RILEY, 1964; MALOTKY and ANDERSON, 1976). Scorodite (FeAsO₄·2H₂O) may form under certain circumstances (HAGUE, 1887). STAUFFER *et al.* (1980) noted that Interchange Spring contains dissolved oxygen (0.6 mg L⁻¹ by Winkler), that virtually all the As is

present as As(V), and that the total Fe content of the spring water is at least an order of magnitude higher than for typical alkaline hot springs outside of Norris. Relatively low field pH (6.3 to 6.7) and high concentrations of Al, Fe, and Mn (up to 0.19 mg L⁻¹) have also been reported for the travertine-depositing Terrace Spring (THOMPSON *et al.*, 1975). Arsenic losses have occurred in all these springs.

Conversely, the apparent conservatism of As at Hillside, Mystic Falls, Mammoth, and in the Yellowstone Canyon warm springs appears to result from low redox potential, and, in the first three cases, lack of evidence for Fe and Mn mobilization and subsequent precipitation (*cf.* THOMPSON *et al.*, 1975; STAUFFER *et al.*, 1980).

High Cl/As on Geyser Hill

The high Cl/As ratios on Geyser Hill are unlikely to have resulted from arsenic precipitation in the sub-surface for all of the following reasons: 1) The Cl/As ratio is independent of the manner (hence rate) in which the fluid cooled. In fact, the ratio is constant for the Myriad Group, Geyser Hill, and the boiling discharging springs and geysers at Lone Star Basin. 2) The high pH's and high flux rates for the geysers on Geyser Hill are unfavorable for mineral deposition. This is the basis for the high reservoir temperatures indicated by the silica geothermometer. 3) No arsenic mineral assemblage was found by ALLEN and DAY (1935) in Carnegie #1 drillhole (Myriad Group) nor in any of the detailed mineralogical studies of the 13 more recent scientific drill cores (WHITE *et al.*, 1975; KEITH *et al.*, 1978). 4) Precipitation of arsenic sulfides in the intermediate reservoir feeding all of Geyser Hill is unlikely because FOURNIER *et al.* (1976) estimate that the reservoir temperature exceeds 217°C.

Table 5. Antimony concentrations (mg L⁻¹) and atomic ratios in representative Yellowstone thermal springs.

Spring Name	Sample I.D.	Cl	Sb	Cl/Sb	As/Sb
<u>West Thumb Basin*</u>					
Lake Side	YJ-74-68	301	0.115	9,000	28
Blue Bell	YJ-74-69	304	0.110	9,500	30
Ephedra	YJ-74-70	301	0.107	9,700	31
King	YJ-74-75	261	0.066	13,600	38
Occasional	YJ-74-72	201	0.047	14,700	43
<u>Upper Biscuit Basins[†]</u>					
Old Faithful Seep	YS-74-122	365	0.107	11,700	19
Ear	YT-73-71	403	0.081	17,100	27
Tortoise Shell	YS-74-123	389	0.087	15,400	30
Witches Cauldron	YS-74-125	377	0.057	22,800	43
Spouter	YS-74-127	317	0.045	24,200	54
Bowtie	YS-74-129	314	0.036	30,000	66
Sapphire	YT-73-62	297	0.036	28,400	66
<u>Midway-Lower Basins</u>					
Excelsior Crater	YT-73-76	266	0.066	13,900	48
Octopus	YS-74-112	263	0.058	15,600	41
Gentian Pool	YT-73-68	300	0.098	10,500	41
Azure Pool	YS-74-132	318	0.081	13,500	30
Azure Satellite	YS-74-136	312	0.073	14,700	32
Ojo Caliente	YE-351	331	0.084	13,500	30
<u>North of Madison Junction</u>					
Base Porcelain Terrace	YT-73-74	704	0.047	51,500	98
Little Whirligig	YT-73-61	587	0.064	31,600	91
Blue-Mammoth	YS-74-147	166	0.009	63,000	123
Calcite-Yellowstone	YS-74-144	242	0.054	15,400	44
Joseph's Coat	YH-74	335	0.166	6,900	77

* Lakeside is key indicator spring for West Thumb.

[†] Progression is NW from Geyser Hill to Biscuit Basin.

Thermodynamic data indicate that orpiment precipitation is unlikely at this high temperature. 5) At the lower temperatures (100–150°C) in the periodically discharging geyser reservoirs adiabatic-related pH increases have compensated for temperature decreases, thus maintaining conditions unfavorable for orpiment precipitation. 6) The absence of near surface dilution by meteoric water on Geyser Hill and available information on Eh, dissolved sulfide and arsenic speciation (STAUFFER *et al.*, 1980) preclude precipitation reactions involving As(V). 7) Arsenic co-deposition with amorphous silica is unlikely both because of 1) and 2) above and because STAUFFER *et al.* (1980) found insignificant As losses ($0 \pm 1\%$) accompanying silica losses averaging 23% in two hot spring drainage channels in the Lower Geyser Basin. 8) The As/Sb ratio attains a *minimum* value of 10 at Old Faithful Seep among all the samples tested in Yellowstone Park. Because WHITE (1967) and WEISSBERG (1969) showed that Sb is preferentially precipitated (as compared to As) both at Steamboat Springs and the Broadlands (New Zealand), the high Cl/As ratio on Geyser Hill cannot be due to As precipitation.

Origin of arsenic in geothermal waters

If one accepts the hypothesis that the high Cl, high SiO₂, high Cl/ΣCO₃, high Cl/SO₄ waters at Geyser Hill and Norris are the most representative of the high enthalpy parents feeding the southern and northern park thermal regions, then the large documented decreases in the Cl/As ratio accompanying increased carbonate alkalinity suggest that at least 30 to 50% of the total Park arsenic flux may be of rock leaching origin. Downward shifts in the Cl/ΣCO₃ ratio are of diagnostic value in mapping hot water migrations and rock-water interactions (FOURNIER and TRUESDELL, 1970; TRUESDELL, 1976).

The decreases in the Cl/As ratio with increased bicarbonate underestimate the possible arsenic contribution from wall-rock interactions because some, as yet unidentified, fraction of the total Cl flux may be of rock-leaching origin (ELLIS, 1970; ELLIS and MAHON, 1964, 1967). Previously, ELLIS and MAHON's (1964, 1967) laboratory studies showed that As in geothermal waters is possibly of rock leaching rather than direct magmatic origin. More recently, EWERS (1977) arrived at a similar conclusion. ONISHI and SANDELL's (1955) findings that silicic volcanic rocks and especially volcanic glasses have elevated As contents also lends qualitative support to a secondary rock leaching origin because CHRISTENSEN and BLANK (1972) showed that a thick layer of ash-flow tuff overlies the important thermal regions of the Park.

Arsenic and antimony in geothermal waters outside Yellowstone Park

Recent chemical data from other locations indicate that solubility controls on As are extremely weak or non-existent in undiluted, alkaline, water-dominated

geothermal systems. Individual spring waters in California, Turkey and Chile have As concentrations ranging up to 50 mg L⁻¹, an order of magnitude higher than the Norris (YNP) or Wairakei (New Zealand) samples (Table 6). Despite the very high As concentrations at El Tatio, The Cl/As ratio is relatively uniform; only two of the 21 ratios fall outside the range 310 to 450 (ELLIS, 1969).

Chloride is the principal geochemical correlate of As in all of the explored high temperature igneous systems. The Cl/As ratios for Chile, Yellowstone, Steamboat Springs, Lassen Park, and New Zealand are remarkably similar despite the > order of magnitude variation in Cl concentration. Although the Cl/As ratio generally decreases with decreasing Cl/ΣCO₃ in Yellowstone Park, alkalinity shows little relationship to As in other geothermal systems. Thus, the El Tatio samples combine relatively low Cl/As ratios with very large Cl/ΣCO₃ ratios (ELLIS, 1969; CUSICANQUI *et al.*, 1976). El Tatio is near saturation with respect to calcite (CUSICANQUI *et al.*, 1976).

Partial As losses from solution following large scale dilution by meteoric water have also been reported for other geothermal fields. Examples include Champagne Pool (Wairakei, New Zealand; *cf.* ELLIS, 1973), and the dilute warm springs in Long Valley, California (*cf.* WILLEY *et al.*, 1974; FOURNIER *et al.*, 1979).

ITCHIE (1961) noted the wide range of Sb concentrations in his survey of New Zealand geothermal waters, and the rarity of Sb concentrations above 0.20 mg L⁻¹. Considering the present Yellowstone, Steamboat, and Lassen samples ensemble, the histo-

Table 6. Arsenic and antimony in selected thermal waters outside Yellowstone Park.

Locality, Sample I.D., Reference	Cl	As	Sb	Cl/As	Cl/Sb
	(mg/l)			Atomic	
<u>Steamboat Springs, Nevada</u>					
SBJ-75-1 June 1975 ^P	769	2.980	0.257	564	10,700
SBJ-75-4 June 1975 ^P	795	2.900	0.094	578	29,100
#12* April 1950 ^a	944	3.100	0.40	643	8,100
#5* April 1950 ^a	920	2.900	0.10	669	31,600
SBT-74-2 1974 ^P	852	3.070	---	586	---
SBT-74-3 1974 ^P	930	3.310	---	593	---
SBT-74-50 1974 ^P	719	2.100	---	722	---
<u>Lassen Peak - Tehama Co., California</u>					
LAJ-75-1 Growler, 1975 ^P	2273	11.00	0.47	437	16,600
LAJ-75-2 Morgan, 1975 ^P	2313	24.30	0.65	201	12,200
Morgan, July 1949 ^D	2427	2.20	0.0	2300	---
<u>Outside USA</u>					
Drillhole KD1a Kizildere, Turkey ^e	117	39.0	---	6.33	---
El Tatio, Chile ^c Spring #226*	8233	47.0	---	370	---
El Tatio, Chile ^c Spring #227*	8220	46.0	---	377	---
Drillhole 24, Wairakei ^e New Zealand	2210	4.5	---	1040	---
Drillhole 8, Broadlands ^e New Zealand	1750	5.7	---	648	---

Notes: a - analyses by Brannock, U.S.G.S., reported in White (1967).

b - spectrographic analyses by U.S.G.S., reported in White (1957).

c - Ellis (1969), Cusicanqui *et al.* (1976).

e - reported in Ellis (1973).

p - geochemical results from present work.

* Highest Cl waters for Steamboat Springs and El Tatio selected for the comparison.

gram for Sb in thermal waters of the western USA is almost indistinguishable from that of New Zealand.

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