



Hydrogeochemistry and geothermal potential of Montezuma Hot Springs, New Mexico

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2015, pp. 289-302. <https://doi.org/10.56577/FFC-66.289>

Supplemental data: <https://nmgs.nmt.edu/repository/index.cfm?rid=2015005>

in:

Guidebook 66 - Geology of the Las Vegas Area, Lindline, Jennifer; Petronis, Michael; Zebrowski, Joseph, New Mexico Geological Society 66th Annual Fall Field Conference Guidebook, 312 p. <https://doi.org/10.56577/FFC-66>

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HYDROGEOCHEMISTRY AND GEOTHERMAL POTENTIAL OF MONTEZUMA HOT SPRINGS, NEW MEXICO

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ABSTRACT—The Montezuma Hot Springs discharge relatively dilute Na-Cl-HCO₃-SO₄ fluid having moderate silica contents (≤ 80 ppm SiO₂) and amazingly high fluoride contents (up to 23 ppm F). There is no geochemical indication that the hot spring fluid is derived from a more concentrated, high-temperature ($\geq 150^\circ\text{C}$) reservoir fluid. Stable isotope relations show that the hot spring fluids are composed of local meteoric water. Tritium data show that the hot spring fluids are at least 50 to 70 years old based on a simple “piston-flow” model, and possibly several thousand years old based on a more complicated “well-mixed” model. The $^3\text{He}/^4\text{He}$ R/R_A value of hot spring fluid is only 0.083, indicating that there is virtually no primordial helium in the hot spring fluids and that there is no magmatic heat source for the underlying reservoir. The springs issue from crushed and fractured rocks at the intersection of the Montezuma Fault and the Rio Gallinas, and therefore fit a deep fault circulation conceptual model. Using a standard suite of chemical geothermometers, a reasonable estimate of the maximum reservoir temperature is about 115°C and a minimum reservoir temperature is about 90°C . Using a mass balance approach and a crude estimate of flow rate in the Rio Gallinas (September 1995), the estimated total discharge rate of end-member fluid from the Montezuma Hot Springs is 180 l/min ($\pm 30\%$).

INTRODUCTION

This paper provides a geothermal resource interpretation of hydrogeochemical data from Montezuma Hot Springs, New Mexico (Fig. 1). The authors obtained the data from 1987 to present. Samples acquired in 1993 through 1995 were collected to provide information for a failed Hot Dry Rock geothermal project conducted by Los Alamos National Laboratory for the benefit of the United World College (Nickerson, 1995). These data have not been previously published. Another geothermal assessment was conducted in the mid-1990s by Witcher (1997). Based on these earlier results and our own evaluation, we believe the Montezuma Hot Springs issue from an intermediate temperature (roughly 115°C) geothermal resource of small to modest size that could be used for a rebuilt spa, and/or very small-scale green housing or aqua culture. The resource is not hot or large enough to effectively generate electric power or provide space heat for the United World College.

MONTEZUMA HOT SPRINGS

Roughly 20 to 30 hot springs and seeps ($\leq 55^\circ\text{C}$) discharge along the banks of Gallinas Creek (Rio Gallinas) about 10 km WNW of Las Vegas, New Mexico (Fig. 2). Initially, the springs were used for bathing and clothes washing (see historical details in Summers, 1976). In the late 1800s, the springs were developed into a fancy resort and spa after a large Victorian style hotel (referred to as the Montezuma Castle) was built on the property. By the mid-1900s, the resort and hotel met financial hard times. In 1981, American tycoon Armand Hammer bought the scenic and historic property and converted it into one of many United World Colleges. In 1997, the National Trust for Historic Preservation placed the old “castle” on the list of America’s Most Endangered Historic Places. In 2000–2001, the college invested

\$10.5 million dollars into restoration and “The Castle” became the Davis International Center. The UWC continues to allow free bathing in the hot springs for the local populace.

Summers (1976) provides a summary of previous work on the hot springs including some early geochemistry, and a good map of the spring area circa 1960. The geology of the area was mapped in detail by Baltz (1972). Bejnar and Bejnar (1979) recounted another interesting history of the area, added some structural geology and offered an early geothermal assessment.

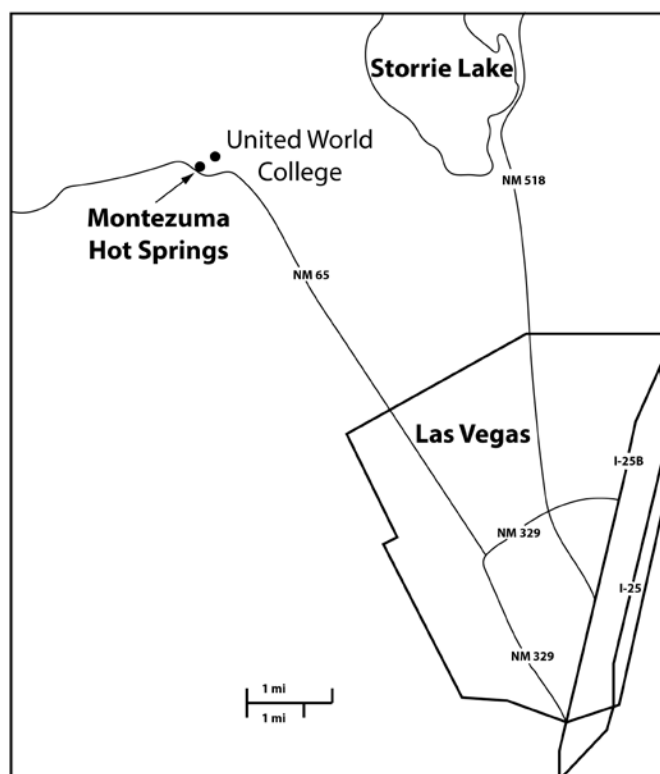


FIGURE 1. Map showing location of Montezuma Hot Springs with respect to major roads, the city of Las Vegas, and the United World College.

Witcher (1997) outlined a geothermal model of the hot spring system. Later, Witcher (2007) indicated that the spring system is associated with the convergent margin of a Laramide basement-cored uplift, a common structural feature of many New Mexico geothermal systems. The heat flow is estimated at about 105 ± 20 mW/m² (2.3 ± 0.5 HFU) with an average geothermal gradient of about 50°C/km over an area of at least 100 km² (Reiter et al., 1979, fig. 1 and tables).

The springs and seeps issue primarily from a boggy slope on the south side of the Rio Gallinas. A few seeps can also be found on the north bank. The entire thermal area extends for about 500 m along the river. Through time, estimates on the number of thermal features vary from about 20 to 40 with temperatures ranging from “tepid” to 60°C. From 1982 to present, we visited the site several times, examining roughly 20 thermal features and two defunct wells. The maximum measured discharge temperature was 55°C. The original bathhouses, pools and other structures are in ruins. Invariably, local residents were bathing in the better spring sites, many of which had been re-engineered with shovels and concrete to create small canals to bathing pools. Significantly, there are no hot spring deposits such as sinter or travertine, and none of the springs or seeps discharged free gas at the times we visited the area, although some springs occasionally release small bursts of what appears to be mostly air. One previous investigator

(around 1875) mentions a “trace of hydrogen sulfide hardly perceptible by odor,” but we have not reliably detected this smell. In early November 2014, we re-examined the site and measured the temperature and flow rates of the largest springs that were accessible (Table 1 and Figs. 3A to 3J). The total flow of these sites was ≤ 57 l/min. We could not access the spring in the Main Bathhouse because it was barred and locked (Fig. 3J).

Geologically, the rocks east of the springs consist of steeply dipping Devonian through Cretaceous sedimentary strata folded into a spectacular series of north-trending hogbacks (e.g., Fig. 4). The sedimentary beds dip 60° east to vertical. In some locations, the beds are overturned. These folded rocks are in fault contact to the west with relatively undeformed Precambrian granitic and metamorphic rocks along the Montezuma Fault (Fig. 2). Mostly flat lying Paleozoic rocks overlie the Precambrian. The springs issue from crushed and fractured rocks at the intersection of the Montezuma Fault and the Rio Gallinas (Fig. 3D). Shattered Precambrian rocks are visible in several locations along the river and the adjacent highway in the vicinity of the springs. Displacement along the fault is at least 610 m, down to the east. The Rio Gallinas flows southeast, cutting across the faulted and folded rocks, but does not appear to be fault-controlled. Significantly, there is little to no hydrothermal alteration of the faulted and folded rocks.

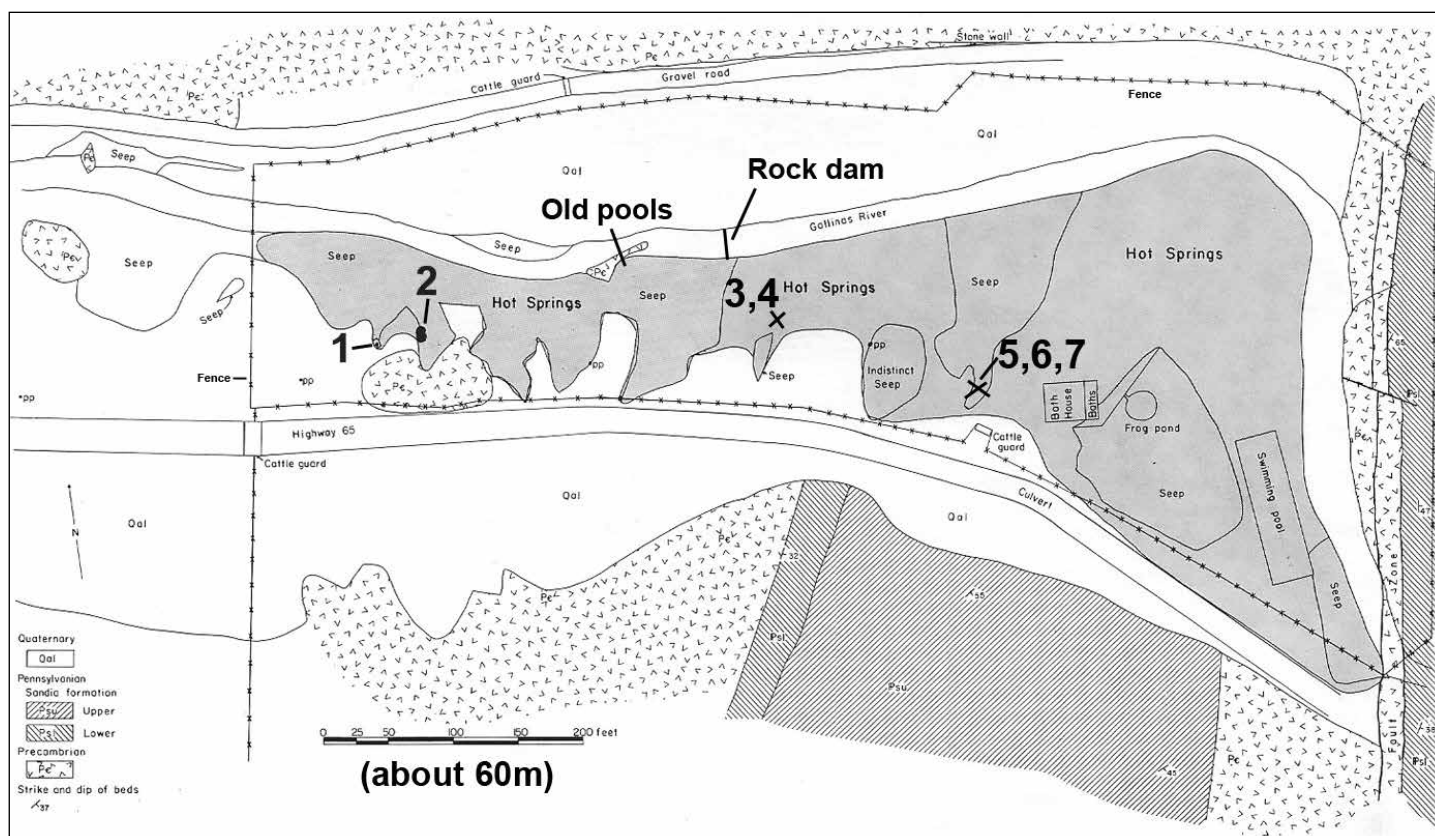


FIGURE 2. Map of Montezuma Hot Springs (modified from Summers, 1976, fig. 47) showing locations of springs and seeps, the old bathhouse, the geology, and sites examined in November 2014 (Table 1). Fault zone labeled on extreme right side of figure refers to the north-trending Montezuma Fault Zone.

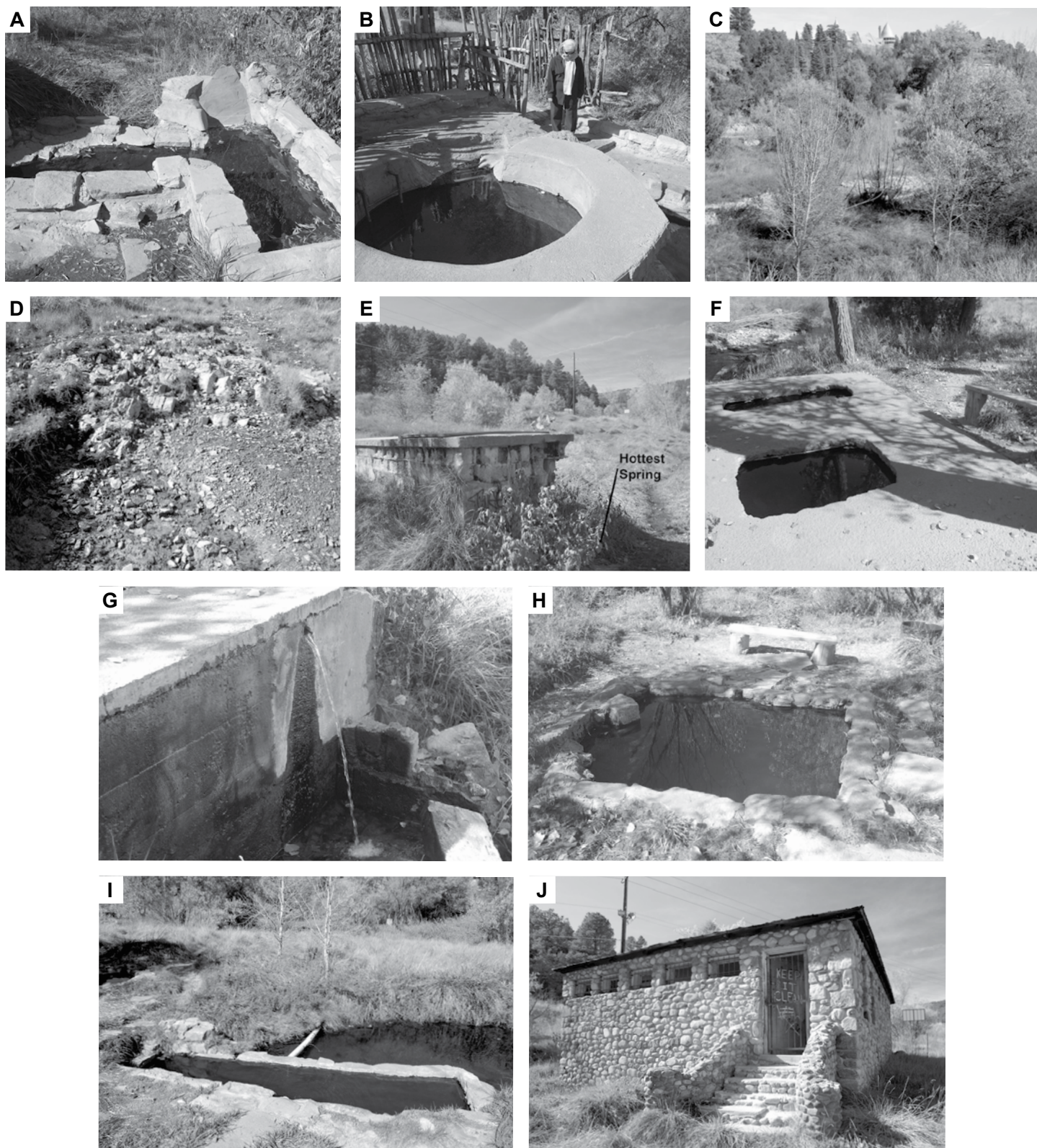


FIGURE 3. Photos of Montezuma Hot Springs in November 2014 (see also Table 1): A. Small bathing pool, site 1; B. Large cascading bathing pools at site 2, called St. Michael's Spring by local bathers in the mid-1990s; C. View from site 2 across Rio Gallinas to the Montezuma Castle; D. Fractured Precambrian rocks in the seep east of site 2; E. View WSW at old concrete crib or tank that presently hosts the "hottest spring" measureable in November 2014 (site 3, 53.9°C); F. Two soaking pools and bench constitute site 4 just NE of site 3; G. Discharge from site 4 was measured at 10.0 l/min; H. Bathing pool at site 5 west of old bathhouse; I. Long bathing pool, site 7, collects overflow from sites 5 and 6; J. Entrance to old bathhouse which is now barred and locked. Several samples in excess of 54°C were collected from here in the 1990s. (See also Color Plate 4)

METHODS

Sampling methods of spring and well waters follow those described in Goff et al. (2001). Temperatures were obtained with a calibrated digital thermometer and field pH was measured with pH sensitive papers. Flow rates of springs were estimated visually or obtained with a 1-liter beaker and stopwatch. A 125-ml plastic bottle of filtered (0.45 μ), unacidified water was collected for anions; a 125-ml plastic bottle of filtered water, acidified in the field to pH ≤ 2 with spectrographically pure HNO₃, was collected for cations, silica, and trace metals; a 30-ml glass bottle of raw water was filled for deuterium/oxygen-18 stable isotope measurements; a 500-ml glass bottle of raw water was filled for tritium analysis. Glass bottles were fitted with polyseal caps. One sample of water was collected in 1997 for noble gas analysis by flowing spring water for several minutes through a copper tube and closing the ends off with refrigerator clamps. Basic field data for the hot springs are listed in Tables 1 and 2.

Water analyses were performed by D. Counce at Los Alamos National Laboratory using a variety of methods (see table 2 in Goff et al., 2001). Southern Methodist University and the Tritium Laboratory, University of Miami provided stable isotope and tritium results, respectively. The single noble gas sample was analyzed by R. Poreda, University of Rochester.

CHEMISTRY

Tables 3 and 4 list chemical analyses of several Montezuma Hot Spring samples collected since 1987 with a few earlier Montezuma analyses, and compare these results to those from a known high-temperature geothermal system, the Valles caldera, New Mexico. Montezuma Hot Spring waters are considerably more potent in dissolved constituents than typical potable water, represented by Rio Gallinas. However, compared to many other geothermal fluids, Montezuma springs are relatively dilute Na-Cl-HCO₃-SO₄ waters (TDS ≤ 580 ppm) having moderate silica contents (≤ 80 ppm SiO₂) and amazingly high fluoride contents (≤ 23 ppm F!). Compared to high-temperature geothermal fluids ($\leq 300^\circ\text{C}$) such as those at Valles caldera, Montezuma Hot Spring waters contain substantially less Cl and more relative HCO₃ and SO₄ (Fig. 5).

Excess F in Montezuma fluids probably originates from dissolution of host Precambrian rock, which contains hornblende, biotite and apatite in this area (Summers, 1976; S. Kelley, personal commun., 2015). These minerals occasionally contain high relative F that can be leached by groundwater. In any event, such high F contents pose a minor health hazard because the water is not suitable for drinking without treatment or dilution. The current maximum contaminant level (MCL) of F allowed in drinking



FIGURE 4. East-dipping Paleozoic rocks are exposed along south side of highway just east of the hot springs. Minor faults cut the layering in the lower half of the outcrop.

TABLE 1. Temperatures and flow rates of principal springs at Montezuma Hot Springs, November 2014.

Location (Fig. 1)	Maximum Temp. (°C)	Flow Rate (l/min)	Notes
Site 1	43.2	4.5	Temperature measured in tank to left of pool, Fig. 3A.
Site 2	46.7	13.2	Uppermost pool; called St Michaels Spring in the mid-1990s
Site 3	53.9	≤2	NW corner of concrete tank, Fig. 3E.
Site 4	45.1	10.0	Total flow of site 4, Figs. 3F and 3G.
Site 5	40.8	≤3	Pool nearest footpath; intermittent gas
Site 6	42.6	10.7	Uppermost pool
Site 7	41.0	13.3	Collective input from sites 5 and 6, Fig. 3I.
Total		≤56.7	Total of major springs

TABLE 2. Basic field data for Montezuma Hot Springs, New Mexico. Data not available indicated by "na."

Sample No	Name	Date	Description	Temp	Field pH	Flow Rate (l/min)	Notes
NNM-5	Well "25"	12/3/87	Well "25" is on the north side of river near old coal plant.	44.0	6.3	none	Sample taken from well using a glass pop bottle on parachute cord as bailer.
NNM93-1	Main Bathhouse	6/8/93	Bathhouse more-or-less in ruins.	55.1	8.0	20 - 40	From discharge in bathhouse.
NNM93-2	St Michael's Spg	6/8/93	Name comes from local population of bathers.	46.7	8.0	11, measured	Spring discharges near south edge of river, west end of main spring group.
NNM93-3	Central Spg Tank	6/8/93	Central holding tank for main group of springs.	53.9	7.5	≤11	Tank contents are dominated by discharge of Main Bathhouse spring.
NNM93-4	Gallinas River	6/8/93	Gallinas Riv, 3.2 km upstream.	na	na	na	Sample taken for isotopes.
NNM93-5	Gallinas River	6/8/93	Gallinas Riv. Just below springs.	na	na	na	Sample taken for isotopes.
UWC94-1	Main Bathhouse	6/22/94	No change from 1993.	54.5	8.9	20 - 40	No change from 1993.
UWC94-2	Central Spg Tank	6/22/94	No change from 1993.	54.0	9.1	12	No change from 1993.
UWC94-3	Unnamed seep	6/22/94	South edge of river below highway near survey marker	42.0	9.1	≤3	Collected to see if it is mixed water.
UWC94-31	River above springs	8/4/94	Collected about 50 m upstream of first observable spring.	na	na	na	Collected as background sample.
UWC94-33	Main Bathhouse	8/4/94	No change from 1993.	na	na	na	No change from 1993.
NNM95-1	Unnamed spring	9/21/95	Collected upstream of main springs.	40.8	7.5	4	Issues from fractured Precambrian rocks.
NNM95-2	River below springs	9/21/95	Collected 50 m downstream of springs.	14.4	7.5	1900	Collected for mass balance calculations.
NNM95-3	"New" spring	9/21/95	Supposedly a new spring found by UWC manager.	46.1	7.5	19	Collected only because it was supposedly new.
NNM95-4	Main Bathhouse	9/21/95	No change from 1993.	54.1	8.0	20, measured	Little change from 1993.
NNM95-5	River above springs	9/21/95	Collected about 50 m upstream of first observable spring.	13.4	8.0	na	Collected for mass balance calculations.
NNM97-1	Main Bathhouse	10/14/97	No obvious change from 1995.	55.1	na	na	Collected for noble gases only.
Comparison of Montezuma hot spring fluids with Valles caldera high-temperature geothermal fluids.							
BA-5	Well Baca-4	7/2/82	From Bandelier Tuff between 2000 and 6000 ft.	297	na	na	Sample collected during flow test of well using min-separator.
VC2B-90	Well VC-2B	1/17/90	From single fracture, Precambrian intrusive, 5760 ft.	295	na	na	Sample collected with special high-temperature <i>in situ</i> sampler.

water within the United States is 4.0 ppm (U.S. EPA, 2013), about 1/6 the maximum level analyzed at Montezuma Hot Springs.

Because calcium contents of the spring waters are low but fluoride is high, we believe they are nearly in equilibrium with the mineral fluorite (CaF_2). This can be evaluated without use of an equilibrium code in the following way. The solubility product (K_{sp}) of fluorite in pure water is defined as:

$$K_{sp} = [\text{Ca}^{+2}] \times [\text{F}^{-}]^2,$$

and a value of $10^{-10.5}$ mol/liter at 25°C (or 3.2×10^{-10}) is listed in Brownlow (1979, p. 137). We can rearrange the above equation and solve for the fluoride concentration of the end-member, hottest fluids at Montezuma Hot Springs by using a rough value of 4 ppm Ca. This results in a calculated value of 11 ppm F or about half the analyzed value. However, examination of chemical tables shows that fluorite solubility increases with temperature (CRC, 1984, p. B82) and that other divalent salts of fluoride are also relatively insoluble (i.e., MgF_2 , SrF_2). If we assume the *effective* concentration of Ca is 4.5 ppm (see Brownlow, 1979) and that K_{sp} at 55°C increases to 0.15×10^{-9} mol/liter the calculated

TABLE 3. Major and trace element chemistry of geothermal exploration interest, Montezuma Hot Springs, New Mexico (see Goff and Janik, 2000 for explanation of this list); values in ppm unless noted. Data not available indicated by "na."

Name	Sample No	Date	Temp (°C)	pH (lab)	Conduc-tivity	SiO ₂	Ca	Mg	Sr	Na	K	Li	F	Cl	Br	HCO ₃	CO ₃	SO ₄	As	B	TDS	Cat-ions	Bal-ance	
Data of Fraser Goff (Los Alamos Nat'l Lab, 1987 to 1995)																								
Well "25"	NNM-5	12/3/87	44.0	7.98	851	65	3.5	0.06	0.13	182	5.4	0.40	18.5	148	0.6	111	0	44.9	<0.05	0.46	580.5	8.295	7.911	4.73
Main Bathhouse	NNM93-1	6/8/93	55.1	9.03	869	73	3.94	0.09	0.19	177	5.58	0.36	21.3	175	0.81	59.8	18.2	42.8	<0.05	0.55	578.8	8.112	8.531	-5.03
St Michael's Spg	NNM93-2	6/8/93	46.7	8.99	875	65	3.45	0.04	0.13	170	5.70	0.33	22.6	179	0.96	63.4	17.6	44.7	<0.05	0.53	574.1	7.776	8.792	-12.3
Central Spg Tank	NNM93-3	6/8/93	53.9	8.97	882	65	3.44	0.06	0.16	176	5.78	0.32	22.4	182	0.98	62.8	17.3	45.9	<0.05	0.53	583.2	8.033	8.871	-9.92
Main Bathhouse	UWC94-1	6/22/94	54.5	9.27	878	56.0	2.05	0.07	0.13	187	5.60	0.26	21.5	157	0.79	37.0	40.6	41.2	0.0023	0.51	522.2	8.454	8.403	0.61
Central Spg Tank	UWC94-2	6/22/94	54.0	9.03	870	57.3	1.96	0.03	0.11	174	5.52	0.25	21.8	154	0.74	57.1	20.6	40.5	0.0025	0.51	506.4	7.879	7.983	-1.31
Unnamed seep	UWC94-3	6/22/94	42.0	8.97	869	55.6	2.53	0.09	0.1	177	5.55	0.27	21.3	152	0.73	66.0	18.4	40.1	0.0031	0.51	512.9	8.038	7.965	0.91
Unnamed spring	NNM95-1	9/21/95	40.8	8.95	844	69.3	4.21	0.09	0.15	172	5.67	0.34	19.3	150	0.78	65.7	15.4	48.5	0.002	0.49	552.4	7.902	7.875	0.34
River below springs	NNM95-2	9/21/95	14.4	8.24	321	15.8	39.8	3.41	0.12	21.5	1.24	0.04	2.24	17.8	0.07	128	7.5	14.4	<0.001	0.07	252.2	3.257	3.272	-0.44
"New" spring	NNM95-3	9/21/95	46.1	8.78	863	71.0	6.91	0.22	0.15	172	5.93	0.34	20.5	152	0.74	77.1	13.2	46.5	0.002	0.49	567.9	8.093	8.063	0.37
Main Bathhouse	NNM95-4	9/21/95	54.1	8.99	864	71.3	3.67	0.05	0.13	174	5.71	0.34	21.0	157	0.76	60.1	18.0	41.5	0.002	0.50	554.3	7.960	8.009	-0.61
River above springs	NNM95-5	9/21/95	13.4	8.05	259	10.4	43.3	3.71	0.12	5.32	0.89	<0.01	0.31	2.76	<0.02	129	9.0	10.9	<0.001	0.02	215.8	2.732	2.736	-0.15
Selected data from Summers (1976, p. 69-72 and Table M10)																								
bold highlight means probable bad analysis. Star after temperature means analysis and temperature from different dates.																								
Hot Spring #1	None	1/3/66	≤55.2	8.38	810	80	5	0	na	200	6.9	0.36	3.4?	160	3.6?	82	1	na	0.04?	na	na	na	na	na
Hot Spring #6	None	3/11/52	60*	9.0	876	59	4.5	1.1?	na	na	na	na	20	155	na	66	22	42	na	na	na	na	na	na
Hot Spring #13	None	3/11/52	51.2*	8.8	876	68	4.5	1.0?	na	na	na	na	20	155	na	77	16	42	na	na	na	na	na	na
Comparison with Valles caldera high-temperature geothermal fluids.																								
Valles, Well Baca-4	BA-5	7/2/82	297	7.20	na	542	2.6	<0.01	0.07	1112	200	14.3	4.8	1904	5.2	135	0	35	2	12.8				
Valles, Well VC-2B	VC2B-90	1/17/90	295	5.05	12490	882	78.5	0.76	1.22	2350	700	32.8	5.67	4150	13.6	105	0	7.8	2.7	29.6				

TABLE 4. Additional trace element data for waters at Montezuma Hot Springs, New Mexico; values in ppm. Bold means suspect data by old methods; Cs, I, and Rb are often of geothermal interest. Data not available indicated by "na."

Name	Sample No	Date	Temp (°C)	Ag	Al (total)	Ba	Cd	Co	Cr	Cs	Fe	Hg	I
Data of Fraser Goff (Los Alamos Nat'l Lab, 1987 to 1995)													
Well "25"	NNM-5	12/3/87	44.0	<0.001	<0.05	0.01	0.003	<0.002	<0.002	0.054	0.03	<0.05	<0.1
Main Bathhouse	NNM93-1	6/8/93	55.1	<0.001	<0.05	0.01	<0.001	<0.002	0.003	0.065	0.05	na	<0.01
St Michael's Spg	NNM93-2	6/8/93	46.7	<0.001	<0.05	<0.01	<0.001	<0.002	<0.002	0.061	0.07	na	<0.01
Central Spg Tank	NNM93-3	6/8/93	53.9	<0.001	<0.05	<0.01	<0.001	<0.002	<0.002	0.061	0.05	na	<0.01
Main Bathhouse	UWC94-1	6/22/94	54.5	0.0011	0.24	0.01	<0.0005	<0.002	<0.002	0.067	<0.01	<0.0002	<0.01
Central Spg Tank	UWC94-2	6/22/94	54.0	<0.0005	0.22	<0.01	<0.0005	<0.002	0.07	0.066	0.10	<0.0002	<0.01
Unnamed seep	UWC94-3	6/22/94	42.0	<0.0005	0.18	0.02	<0.0005	<0.002	<0.002	0.06	<0.01	<0.0002	<0.01
Unnamed spring	NNM95-1	9/21/95	40.8	na	0.04	0.03	na	na	na	0.064	<0.01	na	<0.01
River below springs	NNM95-2	9/21/95	14.4	na	0.08	0.04	na	na	na	0.013	0.06	na	<0.01
"New" spring	NNM95-3	9/21/95	46.1	na	0.30	0.03	na	na	na	0.073	0.21	na	<0.01
Main Bathhouse	NNM95-4	9/21/95	54.1	na	0.06	0.01	na	na	na	0.072	<0.01	na	<0.01
River above springs	NNM95-5	9/21/95	13.4	na	0.06	0.04	na	na	na	<0.002	0.03	na	<0.01
Comparison with Valles caldera high-temperature geothermal fluids.													
Valles, Well Baca-13		6/4/82	278	<0.01	0.31	0.02	<0.01	0.02	0.02	na	0.02	na	
Valles, Well VC-2B		1/7/90	295	<0.001	0.40	0.32	<0.002	<0.002	<0.002	5.45	0.47	<0.2	0.21

TABLE 4. (Continued)

Name	Mn	Mo	NH ₄	Ni	NO ₃	NO ₂	Pb	PO ₄	Rb	Sb	Se	S ₂ O ₃	U	Zn
Data of Fraser Goff (Los Alamos Nat'l Lab, 1987 to 1995)														
Well "25"	<0.01	0.013	<0.05	<0.002	0.4	na	<0.002	<0.1	0.15	<0.1	<0.05	<0.1	<0.1	<0.01
Main Bathhouse	0.01	0.009	0.16	0.004	0.01	na	0.002	<0.02	0.081	<0.1	na	0.23	na	0.03
St Michael's Spg	<0.01	0.008	0.14	<0.002	0.03	na	0.003	<0.02	0.082	<0.1	na	0.02	na	0.01
Central Spg Tank	<0.01	0.008	0.05	0.002	0.06	na	0.002	<0.02	0.081	<0.1	na	0.13	na	0.02
Main Bathhouse	<0.01	0.005	0.07	<0.002	<0.02	<0.02	<0.002	<0.05	0.081	<0.0002	<0.0002	<0.01	na	0.01
Central Spg Tank	0.02	0.004	0.04	0.045	<0.02	<0.02	<0.002	<0.05	0.078	<0.0002	<0.0002	<0.01	na	<0.01
Unnamed seep	<0.01	0.005	0.07	0.045	<0.02	<0.02	<0.002	<0.05	0.084	<0.0002	<0.0002	<0.01	na	<0.01
Unnamed spring	<0.01	na	0.05	na	0.16	<0.02	na	<0.05	0.076	na	na	<0.01	na	<0.01
River below springs	<0.01	na	0.05	na	<0.02	<0.02	na	<0.05	0.008	na	na	<0.01	na	<0.01
"New" spring	0.01	na	0.03	na	<0.02	<0.02	na	<0.05	0.075	na	na	<0.01	na	<0.01
Main Bathhouse	<0.01	na	0.03	na	<0.02	<0.02	na	<0.05	0.076	na	na	<0.01	na	<0.01
River above springs	<0.01	na	0.02	na	<0.02	<0.02	na	<0.05	<0.002	na	na	<0.01	na	<0.01
Comparison with Valles caldera high-temperature geothermal fluids.														
Valles, Well Baca-13	0.01	0.02	0.31	0.02	<0.1	na	0.04	<1	3.1	na	na	na	na	<0.01
Valles, Well VC-2B	0.014	<0.002	2.49	<0.002	<0.1	na	<0.004	<0.1	11.5	<0.2	<0.2	9.12	<0.2	<0.02

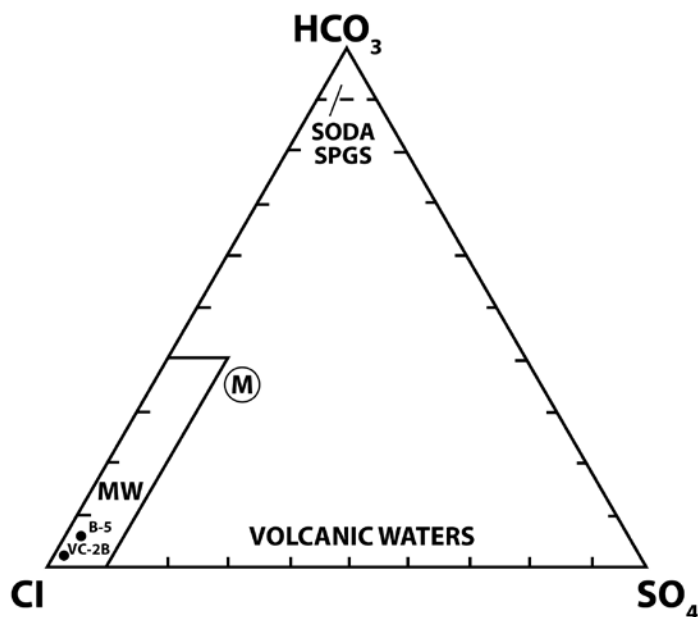


FIGURE 5. Triangular plot of $\text{HCO}_3\text{--SO}_4\text{--Cl}$ (weight basis) comparing end-member fluids of Montezuma Hot Springs (M surrounded by circle) to high-temperature geothermal well fluids from Valles caldera (B-5 and VC-2B). Also shown for comparison is the field for “mature geothermal waters” (MW), the range of typical volcanic waters, and composition of most soda spring waters (modified from Giggenbach, 1992 and Siebe et al., 2007).

value of F is 20.5 ppm, roughly equivalent to the analyzed values. These estimates ignore use of activity coefficients because the hot spring waters are reasonably dilute. Thus, Ca and F concentrations in the hot spring waters are in approximate equilibrium with fluorite, which is observable in small amounts in the Precambrian rocks of the area (S. Kelley, personal commun., 2015).

Other noteworthy geothermal characteristics of the hot waters (Table 3) are low potassium (K) relative to sodium (Na), with a Na/K ratio around 30 (ppm basis), and low contents of key geothermal trace elements arsenic, boron, bromide, and lithium (As, B, Br, and Li). Other trace elements sometimes of note in high-temperature geothermal waters are cesium, iodide, and rubidium (Cs, I and Rb, Table 4) but these constituents are low in Montezuma waters. Compared to Valles caldera geothermal fluids (reservoir temperature $\leq 300^\circ\text{C}$), Montezuma waters are low in all key geothermal elements. Only F contents are higher, but F is not considered to be geothermally significant because F is not uniformly high in most high-temperature geothermal fluids (Goff and Janik, 2000). Additionally, Valles fluids have Na/K ratios of about 3 to 6. Generally, high temperature geothermal fluids have Na/K ratios of 10 or less.

STABLE ISOTOPES

Deuterium and oxygen-18 values of three hot spring samples and two samples of the Rio Gallinas are listed in Table 5. Results are plotted in Figure 6. All hot spring samples cluster in one

location and fall on the World Meteoric Water Line (WMWL) of Craig (1961) and very close to the Santa Fe Meteoric Water Line of Anderholm (1994) indicating that the hot spring system is composed of meteoric water. Both Rio Gallinas samples fall on or near the lines. The sample of river water collected downstream of the hot springs can be explained by mixing upstream river water with hot spring water and lower elevation side stream waters. Because the isotopic composition of the hot spring waters is relatively enriched (higher values) compared to the Rio Gallinas, the Montezuma Hot Springs are recharged at lower elevations than the Rio Gallinas. Probably the recharge of the hot springs is relatively local, whereas the recharge to the river occurs in the higher elevations of the Sangre de Cristo range west of the hot spring system (see Hoefs, 1973 or Rollinson, 1993 for summaries of the effects of elevation, latitude and weather patterns on the isotopic composition of meteoric waters).

Importantly, the hot spring samples show absolutely no oxygen-18 isotope shift to the right of the two meteoric water lines (a shift to higher oxygen-18) caused by high-temperature isotopic exchange between local meteoric water and rocks enriched in oxygen-18 (Craig et al., 1956; Goff and Janik, 2000). Oxygen-18 shifts are influenced by time as well as equilibrium temperature and the isotopic composition of host rocks. Generally speaking, water-rock isotopic exchange occurs at temperatures in excess of 200°C . Consequently, we can assume that reservoir fluids in the Montezuma geothermal system have never experienced high-temperature conditions.

By comparison, the Valles caldera geothermal system (roughly $250\text{--}300^\circ\text{C}$) contains reservoir fluids with oxygen-18 shifts of +2 to +6 ‰ $\delta^{18}\text{O}$ compared to local meteoric water (Goff and Gardner, 1994). The reservoir fluids are similar in deuterium to local meteoric water in the Valles region (Fig. 4) because the reservoir rocks do not contain deuterium for exchange with water.

TRITIUM

Tritium (^3H), the radioactive isotope of hydrogen, has a half-life of 12.4 years and was produced in copious amounts during atmospheric nuclear testing during the 1950s and early 1960s. Atmospheric nuclear testing ceased in 1963. Whereas the “pre-bomb” background value of tritium in local meteoric waters averaged roughly 6 TU (tritium units) before 1950, the bomb induced (anthropogenic) background of tritium climbed to over 6000 TU by 1964 (Vuataz and Goff, 1986). This anthropogenic tritium spike has been decaying since that time and background tritium values have more or less returned to pre-bomb levels at the present time.

Three samples of Montezuma Hot Spring waters collected in 1993–1994 contained about 0.14 to 0.34 TU (Table 5), well below the pre-bomb background values for New Mexico of 6 TU. In contrast, a sample of the Rio Gallinas collected in 1994 had a value of 11.8 TU or about twice the pre-bomb value. We can conclude that the hot spring system contains water that is relatively old compared to local meteoric water but that the Rio Gallinas contains a significant fraction of water younger than the date at which atmospheric nuclear testing began.

TABLE 5. Isotope data from Montezuma Hot Springs, New Mexico.

Name	Sample No	Date	Elev (m)	Temp (°C)	Deuterium (per mil SMOW)	Oxygen-18 (per mil SMOW)	Tritium (TU)	PF age years	WM age years	³ He/ ⁴ He R/R _A	He	He/Ne	Ar	⁴⁰ Ar/ ³⁶ Ar
Data of Fraser Goff (Los Alamos Nat'l Lab, 1987 to 1995)														
Well "25"	NNM-5	12/3/87	2060	44.0	-74.4	-10.46								
Main Bathhouse	NNM93-1	6/8/93	2060	55.1	-74.8	-10.65	0.18 ±0.09	65	7000					
St Michael's Spg	NNM93-2	6/8/93	2061	46.7	-74.7	-10.46	0.14 ±0.09	70	8000					
Central Spg Tank	NNM93-3	6/8/93	2060	53.9										
Gallinas Riv, 2 mi up	NNM93-4	6/8/93	2150	cold	-99.2	-13.51								
Gallinas Riv. Just below	NNM93-5	6/8/93	2050	cold	-86.0	-12.46								
Main Bathhouse	UWC94-1	6/22/94	2060	54.5										
Central Spg Tank	UWC94-2	6/22/94	2060	54.0										
Unnamed seep	UWC94-3	6/22/94	2057	42.0										
River above springs	UWC94-31	8/4/94	2060	cold			11.8 ±0.4	10.5	80					
Main Bathhouse	UWC94-33	8/4/94	2060	54.8			0.34 ±0.09	50	4400					
Unnamed spring	NNM95-1	9/21/95	2057	40.8										
River below springs	NNM95-2	9/21/95	2050	14.4										
"New" spring	NNM95-3	9/21/95	2057	46.1										
Main Bathhouse	NNM95-4	9/21/95	2060	54.1										
River above springs	NNM95-5	9/21/95	2065	13.4										
Main Bathhouse	NNM98-1	10/14/97	2060	55.1						0.0826	0.1648	1038	0.2092	327.5

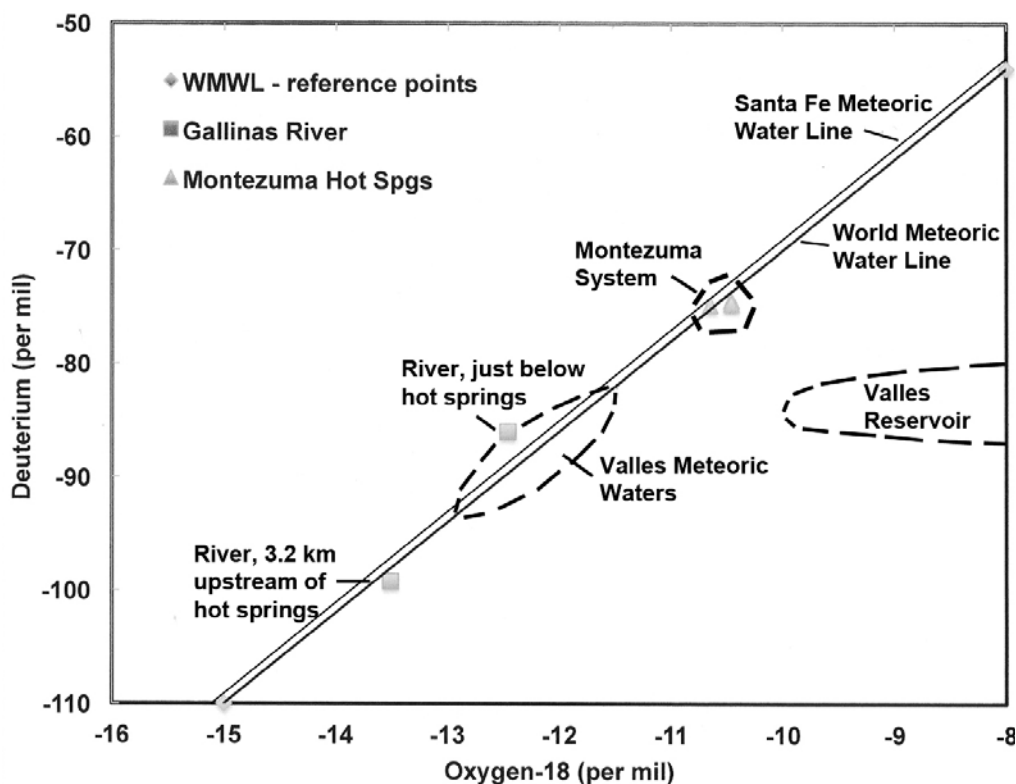


FIGURE 6. Plot of deuterium versus oxygen-18 for Montezuma Hot Springs and the Gallinas River compared to local meteoric waters and high-temperature geothermal fluids of the Valles caldera. Montezuma fluids plot on the World Meteoric Water Line ($\delta D = 8\delta^{18}O + 10$) showing no high-temperature isotope shift in oxygen-18. In contrast, Valles reservoir fluids (210–300°C) have an isotope shift of +2 to +6 permil in oxygen-18. Also shown is the Santa Fe Meteoric Water Line ($\delta D = 8\delta^{18}O + 11.1$) of Anderholm (1994).

10.5 years in 1994, which indicates that the river contains a significant amount of subsurface (older groundwater) input (Vuataz and Goff, 1986).

HELIUM ISOTOPES

The single sample collected from the hottest spring for noble gas work contained surprisingly high dissolved He (0.165 cc/kg), nearly twice the equilibrium solubility value of He in cold water (0.094 cc/kg; CRC, 1984, p. B99) and nearly as much He as Ar (Table 5). The sample He concentration is so large that it falls well outside the usual calibration range of the analysts equipment (R. Poreda, personal commun., 1998). Helium isotope values are reported as R/R_A , where R is the ratio of $^3\text{He}/^4\text{He}$ in the sample and R_A is the ratio of $^3\text{He}/^4\text{He}$ in air. At Montezuma Hot Spring, the sample contains very low primordial ^3He , as indicated by a R/R_A value of only 0.083. This value is much less than the ratio of air (standardized at a ratio of 1) and substantially less than typical values of $8 \pm 2 R/R_A$ measured at most arc volcanoes (see Wehlan et al., 1988 for a summary). By comparison, the $^3\text{He}/^4\text{He}$ ratios of hydrothermal fluids at Valles caldera run from 4 to 6 R/R_A (Goff and Gardner, 1994), and helium ratios in groundwaters from the southern and western Espanola Basin run 0.3 to 2.0 R/R_A (Manning, 2009).

Primordial ^3He originates from the mantle whereas ^4He originates from the crust. The relatively large amount of total He but small $^3\text{He}/^4\text{He}$ ratio in Montezuma Hot Spring water indicates that almost all He originates by radioactive decay of uranium and thorium in Precambrian source rocks, and collects in the springs through fracture flow. There is no reason to suspect, based on helium isotopes, that a deep magma body provides heat to the overlying Montezuma geothermal system.

CHEMICAL GEOTHERMOMETRY

Comments on Chemical Geothermometers

Chemical geothermometers are of two basic types: (1) Those based on absolute concentrations of a constituent in solution, and (2) those based on ratios of two or more constituents in solution. The temperature dependence of silica geothermometers has been calibrated by laboratory experiments under ideal conditions (e.g., Fournier and Rowe, 1966). The solubility of silica polymorphs (i.e., quartz, chalcedony, cristobalite) in pure water as a function of temperature represents the prime example of a laboratory-calibrated geothermometer (Fournier, 1973, 1981). Thus, these are actually geothermometers based on mineral solubilities.

Other geothermometers are determined on empirical relations involving many fluids produced from different geothermal fields where reservoir temperatures are known. In such cases, one or more chemical ratios (usually cation ratios) from production fluids and associated hot spring fluids are plotted against the inverse of reservoir temperature and a linear regression of the data defines the temperature dependence. Thus, empirical geothermometers are highly dependent on the data sets used and boundary conditions on temperature. As a result, there are

at least four different versions of the Na/K geothermometer (Ellis and Mahon, 1967—developed for New Zealand waters; Fournier, 1981—developed for drilled reservoirs worldwide; Truesdell, 1976—uses a combination of previous equations; Giggenbach, 1988—uses mostly reservoir fluids in convergent margin volcanoes). The “best one” depends on how well the calculated temperatures match drilled temperatures within a given reservoir, or more commonly, the previous experience of the investigator. Thus, the best geothermometers to use may be difficult to determine during initial exploration of an undrilled geothermal area.

Table 6 lists the most common chemical geothermometers used on water analyses in geothermal exploration and development. The original equations used for our calculations are listed in the references and can be found in several later texts and research papers (e.g., Powell and Cumming, 2010; Goff and Goff, 2015, Appendix 1). There are several other geothermometers not listed in Table 6 that have been developed for particular situations or geothermal fields. For the Na/K geothermometers, we have listed the Fournier (Na/Kf) and Truesdell (Na/Kt) versions because they generally yield high and low calculated temperatures, respectively, for that ratio.

The empirical geothermometers yield excellent results for reservoirs hosted in young igneous systems such as Valles caldera because these hotter reservoirs have provided most of the data used in the regressions. Most geothermometers have a declared error of ± 20 –30% due to uncertainties in their calibrations and database, and the unknowns associated with rock type, equilibrium, and other variables in each situation of application. The geothermometers are less reliable for tectonic or geopressured geothermal systems of lower reservoir temperature, particularly for fluids of high-Mg content. An exception may be the Li/Mg geothermometers of Kharaka and Mariner (1989) because it uses a database of formation brines in sedimentary basin aquifers. Only one geothermometer in the list (Na-K-Ca, 4/3; Fournier and Truesdell, 1973) works well for cold potable waters (but usually within $\pm 30\%$ of discharge temperature).

By the late 1970s, Fournier was working on a modification of the Na-K-Ca geothermometer that took into account the effect of Mg. Many thermal fluids contain relatively high Mg but the existing geothermometers yielded temperature results known to be too high (i.e., Goff et al., 1977). The Na-K-Ca (Mg-correction) geothermometer of Fournier and Potter (1979) was the first to deal with the Mg problem in a “quantified” manner. The Fournier and Potter equation is complex; Fournier himself recommends a graphical approach after first calculating an “R value” from Mg, Ca and K contents. The delta-T value from the graph is then subtracted from the Na-K-Ca calculation that does not violate the rules of application (1/3 or 4/3).

In our opinion, Fournier (1981) still provides one of the best general discussions on the development, uses, and limitations of chemical geothermometers, although his list of geothermometers is dated. Powell and Cumming (2010) provide access to two Excel spreadsheets that support common graphical analyses of water and gas chemistry, although their bias is toward

high-temperature systems. Please note that dilution, mixing, boiling, precipitation and other reactions can modify original fluid chemistry as temperatures decline during upflow and outflow. As a result, independent indicators of high-temperature should always be sought to support conclusions based on geothermometers. For example, presence of H_2S -rich gases, widespread distribution of boiling Cl -rich springs, and spring deposits of sinter (geyserite, amorphous silica) usually indicate that a reservoir $\geq 150^\circ\text{C}$ lies at depth (Goff and Janik, 2000).

Application to Montezuma Hot Springs

Using the chemistry of Table 3, estimated subsurface reservoir temperatures were calculated and results presented in Table 6. There seems to be pretty good agreement among the quartz, Na/Li and K/Mg equations at a temperature of around 115°C . Among the several silica geothermometers, the quartz equation yields the highest estimated temperatures. If the chemistry presented in Table 3 showed indications of mixing of cold and hot end member compositions, we might conclude that the quartz equation was yielding an intermediate temperature indicative of 'mixing.' However, this is not the case. Thus, the quartz equation is yielding an "upper limit" on the subsurface reservoir temperature at Montezuma. Agreement of Na/Li and K/Mg equations with quartz may be more circumstantial than real because these equations were not created using water compositions such as those at Montezuma.

The chalcedony equation provides a "lower limit" on the probable reservoir temperature at Montezuma Hot Springs. Note that the chalcedony estimate (about 85°C) is similar to that provided by the Na/K equation of Truesdell (about 90°C). The Truesdell equation nearly always yields the lowest of the Na/K temperature estimates (see above). Temperature estimates using the Na/Kf , Na-K-Ca , and Li/Mg equations are probably too high. These geothermometers were not calibrated for intermediate temperature, dilute hot spring fluids such as those at Montezuma and yield temperatures that are 20 to 25°C higher than the quartz equation, which we believe provides the most realistic estimate of an upper temperature limit. The Na-K-Ca (Mg corrected) equation is not applicable to the Montezuma data set because the fluids are so low in dissolved Mg ($<<1$ ppm Mg for end member compositions).

Ternary Geothermometry Plots

Giggenbach (1988) published a ternary plot (Fig. 7A) of $\text{Na}/1000$ - $\text{K}/100$ - $\text{Mg}^{1/2}$ to compare true reservoir fluids with other thermal fluids that he considered to be partially equilibrated, mixed, or "immature." The upper curve on his diagram is defined primarily by his version of the Na/K geothermometer. Tie lines pointing toward the Mg axis supposedly unify mixed fluids of high Mg content with hot end-member fluids. The upper boundary for immature waters is vaguely defined.

When the data of Table 3 are plotted on this diagram, the two Valles reservoir samples clearly plot at more-or-less full equilibrium at 260 to 310°C . However, the average composition of the

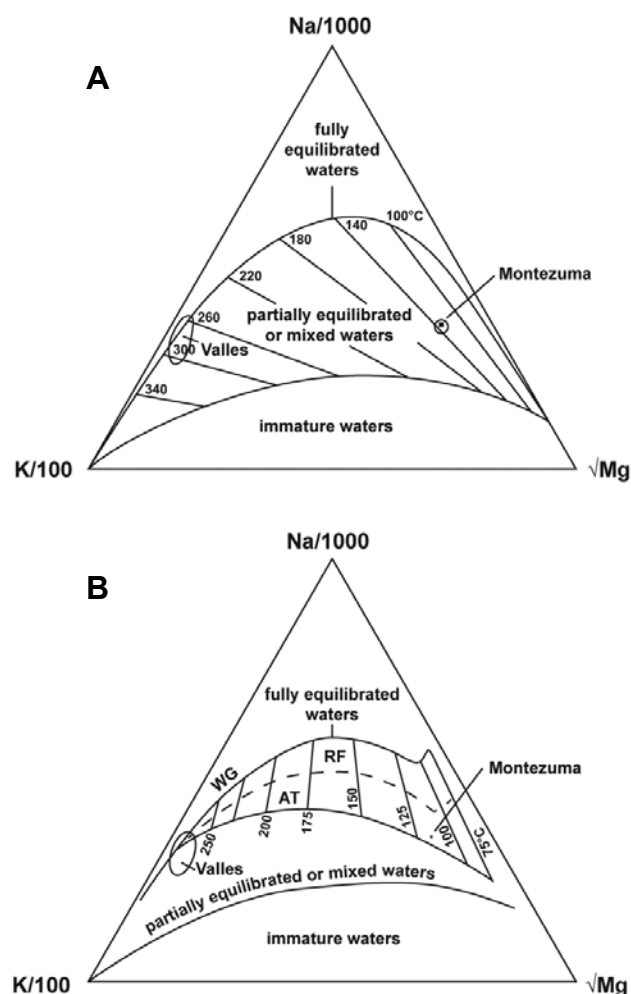


FIGURE 7. Triangular plots of $\text{Na}/1000$, $\text{K}/100$, $\text{Mg}^{1/2}$ showing possible subsurface equilibration temperatures. A. The plot of Giggenbach (1988) and B. The competing plot of Fournier (1990). Montezuma Hot Spring waters plot at $T \leq 140^\circ\text{C}$ on these diagrams as opposed to known high-temperature geothermal fluids from the Valles caldera (260 – 300°C).

hottest Montezuma fluids plot in the field of partial equilibration along a join that is slightly less than 140°C . We see no evidence in the chemistry of Table 3 that the hottest fluids are mixed fluids.

In classic repartee, Fournier (1990) modified Giggenbach's original diagram (Fig. 7B). He noted that the full equilibrium line was dependent on the form of the Na/K equation and so added his and Truesdell's equations to the diagram. Tie lines on this diagram merely compare differences in calculated temperatures among the three equations. Fournier's version of the plot also has a different boundary between immature and partially equilibrated or mixed waters. On this diagram, the two Valles reservoir fluids still appear extremely hot ($>250^\circ\text{C}$), which of course they are. Average Montezuma Hot Spring fluid plots at a temperature of about 110°C in the fully equilibrated field, between the lines defining the Fournier (RF) and the Truesdell (AT) equations.

Our opinion is that these diagrams, although they try to accommodate Mg contents in mixed, partially equilibrated and

“immature” fluids, are not applicable to the Montezuma data set because Mg contents of these fluids are so low. If forced to pick a temperature from these diagrams, we would choose the value of about 110°C on the Fournier plot (Fig. 7B). Based on the 50°C/km temperature gradient determined by Reiter et al. (1979, discussed briefly above), the maximum depth to a resource at 110 to 115°C would be roughly 2 km or a little more, depending on assumptions of average surface temperature.

ESTIMATED DISCHARGE RATE

To the best knowledge of the authors, a satisfactory estimate of total discharge of the Montezuma Hot Springs has not been made before 1970. Using data in Summers (1976), the largest hot spring had a discharge of 79 l/min (20.8 gpm) in 1899. Summers himself measured a total discharge rate of the springs of ≥ 112 l/min (≥ 29.6 gpm) in the 1960s (Summers, 1976). The USGS provided an amazingly high value of 1230 l/min (325 gpm) in 1966, but this estimate is based on temperature differences between the springs and the Rio Gallinas (Summers, 1976).

In September 1995, the first author made an estimate of the total discharge rate of the hot spring system using a chemical mass balance approach (Table 7). The final rate value is highly dependent on the estimate of the flow rate of the Rio Gallinas. On September 21, 1995, the flow of the river was visually observed to be relatively small by merely looking at water levels in the streambed. With the aid of assistants, the width and depth of the river downstream of the hot springs was measured with tapes. The velocity of the river was estimated by floating sticks down river and timing their motion with a stopwatch. From these data, we calculated that the Rio Gallinas on this date was flowing at 1900 l/min (500 gpm) downstream of the hot springs. Our estimated error is about $\pm 20\%$.

For the mass balance calculations, we compared the chemistry of the most concentrated hot spring waters to the chemistry of the Rio Gallinas upstream and downstream of the springs. As can be seen in the data of Table 3, the downstream sample is noticeably affected by the chemistry of the hot springs. Using the chemical values of the most conservative dissolved constituents (Na, K, Li, F, Cl, Br, and B), we calculated the percentage of hot spring water that was in the downstream sample of the Rio Gallinas. The average value is about 9.4%. Combining with the flow rate of the river (1900 l/min), the total discharge rate of end-member hot spring fluid is about 180 l/min (47 gpm) with combined errors of $\pm 30\%$ (a probable value between 125 and 230 l/min (33 and 61 gpm)). Although this estimated total discharge value is relatively crude, it would seem that the USGS value of 1230 l/min (325 gpm) from 1966 is highly overestimated. Using only Cl mass balance, Witcher (1997) estimated a total discharge value of between 83 to 171 gpm for the hot spring system, with the lower value being his preferred value.

CONCLUSIONS

Our investigations of the Montezuma Hot Springs shows that the geothermal system is composed of dilute Na-Cl-HCO₃-SO₄

TABLE 7: Concentration values (ppm) used to determine the percentage discharge into the Gallinas River, September 21, 1995.

Parameter	Gallinas River (downstream)	Gallinas River (upstream)	Difference from thermal input	Average of three springs	Percent from springs
Na	21.5	5.32	16.2	173	9.37
K	1.24	0.89	0.35	5.77	6.07
Li	0.04	0	0.04	0.34	11.8
F	2.24	0.31	1.93	20.3	9.51
Cl	17.8	2.76	15.04	153	9.83
Br	0.07	0	0.07	0.76	9.21
B	0.07	0.02	0.05	0.49	10.1
Average %					9.41

Estimated flow of Gallinas River downstream of hot spring on the above date = roughly 1900 l/min

Estimated total discharge of hot spring system is thus 180 l/min

Previous estimates of discharge (Summers, 1976)

Measured discharge of largest spring = 79 l/min (1899)

Total flow based on temperature difference = 1230 l/min (USGS, 1966)

Total discharge based on measurements = ≥ 112 l/min (1966)

fluid containing moderate silica (≤ 80 ppm SiO₂), amazingly high fluoride (≤ 23 ppm F), and very low concentrations of key geothermal trace elements (As, B, Br, Cs, I, Li, and Rb). Stable isotope results show that the reservoir waters are recharged at relatively low elevation, probably within the local area, and tritium data indicates the waters are probably less than a few hundred years old. Interpretation of chemical geothermometers indicates the maximum subsurface equilibration temperature is probably 115°C. There is no indication of a magmatic heat source but He isotope data indicate circulation in Precambrian crystalline rocks along the Montezuma Fault. Our conceptual model for the system is one of circulation of meteoric water along a deeply penetrating fault zone, more or less similar to that proposed by Witcher (1997). Heat flow and thermal gradient data suggest the geothermal system circulates at a maximum depth of roughly 2 km or a little more. Our measurements of discharge rate using a mass balance approach suggest a total discharge rate of 180 l/min ($\pm 30\%$).

Geothermal systems with high flow rate potential and temperatures of 150°C or more provide potential for electricity generation, whereas systems of lower temperatures are suitable for direct use applications. Our opinion is that the existing reservoir of the Montezuma geothermal system is not capable of generating electric power, but would be capable of small direct use applications (e.g., rebuilt spa, aquaculture, green house) because the water is relatively dilute. Perhaps the latter two applications would make suitable education projects for students of United World College. Because the springs are distributed over a broad area but have relatively low total flow, the various outlets would have to be collected into one pipe for any ambitious effort. Drilling the system for better total flow will probably impact the discharge of the existing hot springs. Due to exceptionally high F contents, the waters must be treated or diluted for potable use.

Future work should include electrical geophysical methods to define structural controls and depth of the resource, more

isotope work on hot and cold fluids, and a better estimate of the discharge rate from precise measurements of flow in the Gallinas River. Measurements of heat generation in local Proterozoic rocks would better constrain heat flow in this area.

ACKNOWLEDGMENTS

Los Alamos National Laboratory funded the field and analytical work performed from 1987 to 1997. Dale Counce (now retired from LANL) provided most of the chemical analyses used in this report. We thank Jim Witcher for a copy of his 1997 report and his endless geothermal wisdom. Shari Kelley (New Mexico Tech) and James A. Stimac (Stimac Geothermal Consulting, Santa Rosa, CA) reviewed the draft manuscript. Jennifer Lindline, NM Highlands University, and Stacy Timmons, New Mexico Bureau of Geology and Mineral Resources, made several editorial improvements to the final manuscript figures, tables and text.

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