Aqueous geochemistry of the Thermopolis hydrothermal system, southern Bighorn Basin, Wyoming, U.S.A.

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ABSTRACT

The Thermopolis hydrothermal system is located in the southern portion of the Bighorn Basin, in and around the town of Thermopolis, in northwest Wyoming. It is the largest hydrothermal system in Wyoming outside of Yellowstone National Park. The system includes hot springs, travertine deposits, and thermal wells. Published models for the hydrothermal system propose the Owl Creek Mountains as the recharge zone, simple conductive heating at depth, and resurfacing of thermal waters up the Thermopolis Anticline.

The geochemistry of the thermal waters of three active hot springs—Big Spring, White Sulphur Spring, and Teepee Fountain—is similar in composition and characteristic of carbonate or carbonate-bearing siliciclastic aquifers. Previous studies of the Thermopolis hydrothermal system postulate that the thermal waters are a mixture of waters from Paleozoic formations. Major element geochemical analyses available for waters from these formations are not of sufficient quality to determine whether the thermal waters are a mixture of the Paleozoic aquifers. In the time frame of this study (one year), the geochemistry of all three springs was constant through all four seasons, spanning spring snowmelt and recharge as well as late-summer and fall dryness. This relationship is consistent with a deep source not influenced by shallow, local hydrogeology. Anomalies are evident in the historic data set for the geochemistry of Big Spring. We speculate that anomalies occurring between 1906 and 1926 suggest mixing of source waters of Big Spring with waters from a siliciclastic formation, and that anomalies occurring between 1926 and 1933 suggest mixing with waters from a formation containing gypsum or anhydrite. Decreased concentrations measured in our study—relative to concentrations measured between 1933 and 1976—may reflect mixing of thermal waters with more dilute waters. Current data are not sufficient to rigorously test these suggestions, and events of sufficient scale taking place in these timeframes have not been identified.

KEY WORDS: Bighorn Basin, hot springs, hydrogeochemistry, hydrothermal system, Thermopolis, Wyoming.

INTRODUCTION

The Thermopolis hydrothermal system is the largest hydrothermal system in Wyoming outside of Yellowstone National Park. Unlike Yellowstone, however, the travertine depositing hot springs of the Thermopolis hydrothermal system are not associated with any obvious volcanic activity; thus, they are considered a non-volcanic hydrothermal system that is partially controlled by regional faulting and fracturing (Hinckley et al., 1982a).

The geology of the Thermopolis area, the area's travertine deposits, and the geochemistry of its hot springs have been studied for more than 100 years.

That being said, the last published quantitative study of Thermopolis waters was completed more than 30 years ago. Here, we present new water analyses for the Thermopolis hydrothermal system that were collected over a one-year period across the seasons between June 2011 and June 2012. Using our new data and historical water analyses of the Thermopolis hydrothermal system, we examine how the system has changed on both seasonal and decadal time scales since 1906. In addition, we use water analyses of formation waters compiled from oil and gas fields to provide a regional context for the Thermopolis hydrothermal system.

BACKGROUND

Regional Geology

The Thermopolis hydrothermal system is located in the southern portion of the Bighorn Basin (Fig. 1), on the northern flank of the east–west trending Owl Creek Mountains (Fig. 1), and along the crest of the west-northwest trending Thermopolis Anticline (Fig. 2). The Thermopolis Anticline stretches for almost 48 km (30 miles) and generally parallels the northern flank of the Owl Creek Mountains. The anticline is segmented into three sections by two north-dipping thrust faults (Paylor et al., 1989). An unnamed syncline separates the Owl Creek Mountains and the Thermopolis Anticline.

The Bighorn Basin is well known for its petroleum systems with many active oil and gas fields surrounding the Thermopolis hydrothermal system (Fig. 2). The Bighorn Dolomite, Madison Limestone, Tensleep Sandstone, and Phosphoria Formation all produce significant quantities of hydrocarbons. These same formations contain large quantities of water, and some also produce large amounts of carbon dioxide (CO_2). Stratigraphic relationships, relative thicknesses, physical descriptions, and general water-bearing characteristics of the formations important to this study are described in Table 1.

The Thermopolis Hydrothermal System

The surface expression of the Thermopolis hydrothermal system includes hot springs, travertine deposits, and thermal wells along the Bighorn River
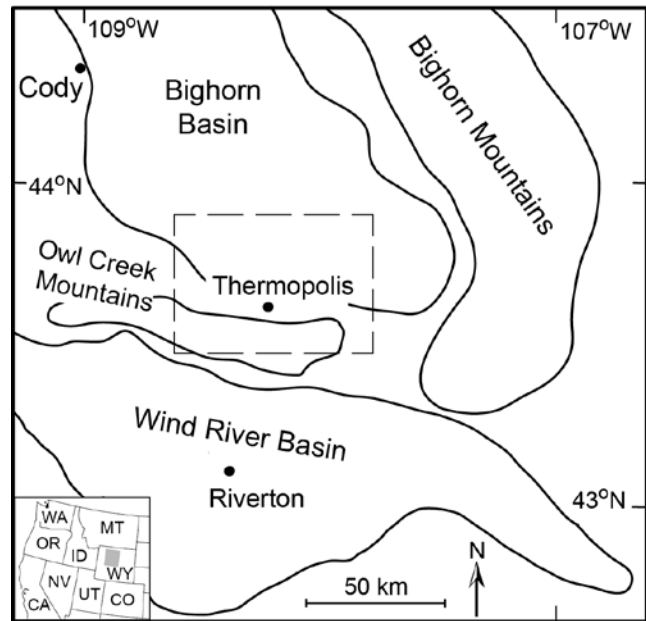

Figure 1. Generalized geologic map of a portion of northern Wyoming showing important sedimentary basins and mountain ranges in the immediate vicinity of Thermopolis, Wyoming. The area of Figure 2 is designated by the dashed box.

on the crest of the Thermopolis Anticline (Fig. 2). All of the hot springs are located inside Hot Springs State Park, within an area of less than five square km (two square miles) (Fig. 3). Two hot springs are active today, Big Spring and White Sulphur Spring. Two additional hot springs—Teepee Fountain and an unnamed spring at the entrance to Hot Springs State Park—are man-made structures fed by Big Spring. Six other hot springs were previously active, but no longer discharge thermal waters; these are Piling Spring, Railroad Spring, Bathtub Spring, Black Sulphur Spring, Terrace Spring, and the Devils Punch Bowl. The cessation of discharge from these springs has been the most notable change in the hydrothermal system in the last century. Privately owned wells located north of Hot Springs State Park (Fig. 3) also produce thermal waters. Detailed descriptions of the hot springs and thermal wells of the Thermopolis hydrothermal system are compiled in Breckenridge and Hinckley (1978) and Hinckley et al. (1982a, b). In the following, we present a brief summary of the hydrothermal system and related travertine deposits.

Travertine deposits are located on the fractured crest of the Thermopolis Anticline along a distance of approximately ten km (six miles) to the west-
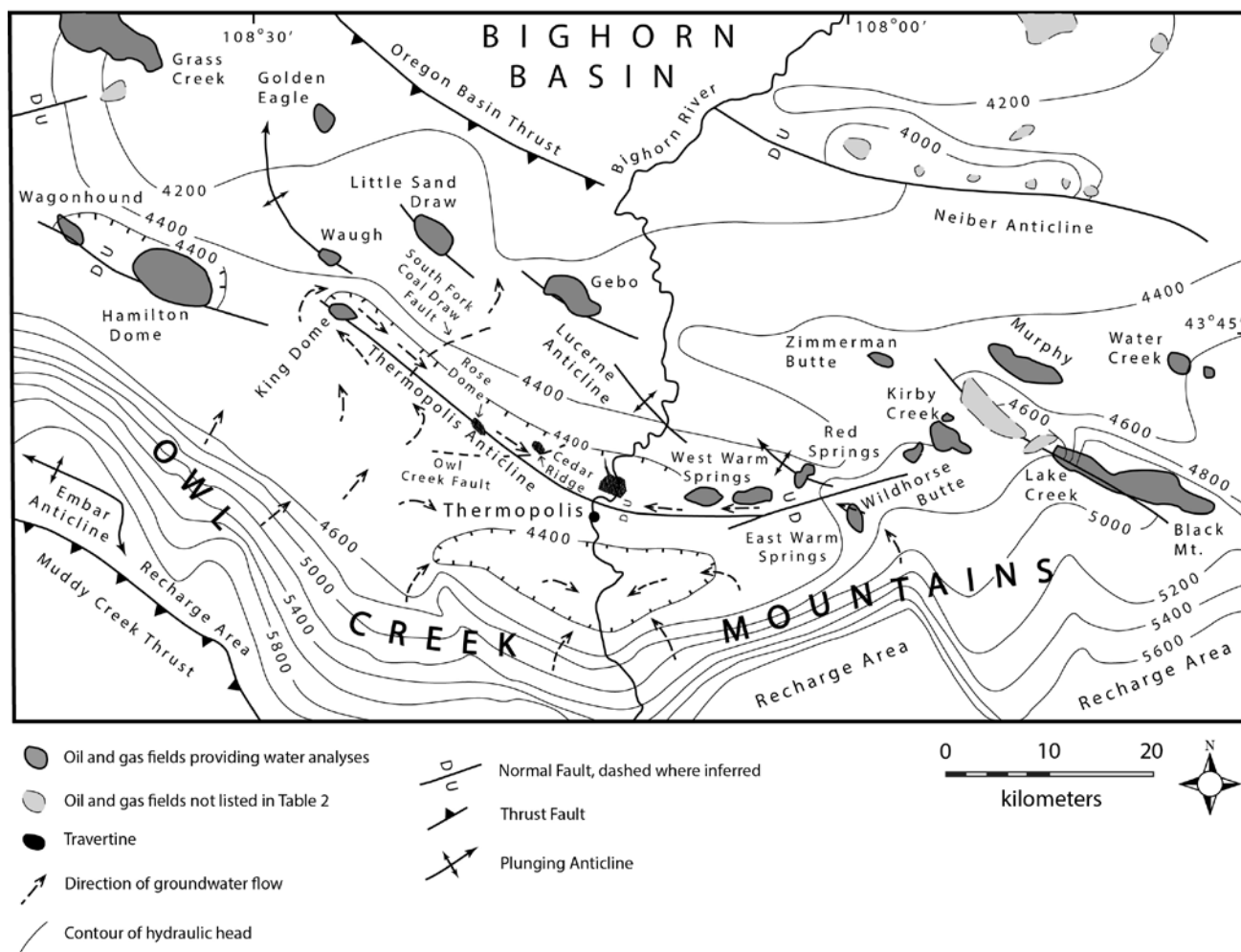
Figure 2. Map depicting the regional geology and hydrology of the Thermopolis hydrothermal system as well as locations of oil and gas fields proximate to the system. Contours are elevations (in feet) of equal hydraulic head in the Park City-Tensleep Aquifer as determined by Huntoon (1993). Dashed arrows illustrate groundwater flow directions based on a model by Jarvis (1986) and Spencer (1986). Information for faults and folds are from Love et al. (1978), Love et al. (1979), and Paylor et al. (1989). Locations of travertine are from Hinckley et al. (1982a). Locations of oil and gas fields are from De Bruin et al. (2004). Hot springs, travertine, and privately-owned thermal wells that are the focus of this study are all located within the town of Thermopolis.

northwest of the Bighorn River (Fig. 2). These outcrops are approximately 100 m (several hundred feet) above the elevation of the river. Travertine outcrops on Round Top and T Hill, for example, lie about 200 m and 100 m (700 feet and 350 feet) above the Bighorn River, respectively. No hot springs are associated with these outcrops; thus, thermal waters must have flowed and deposited travertine along the Thermopolis Anticline in the past. The first published study of the Thermopolis hydrothermal system (Darton, 1906) suggests that travertine deposition may date back to the Tertiary; however, the volume and thickness as well as the age

and stratigraphic relationships of these rocks have not been determined.

The modern hydrothermal system is located within 100 m (a few hundred feet) of the Bighorn River and no more than 10 m (a few tens of feet) above the level of the river. The system is capped by the Triassic Chugwater Formation (Table 1) (Hinckley et al., 1982a). Thermal waters emanate from the Chugwater Formation, and water wells that produce thermal waters penetrate this formation.

Big Spring is the largest and deepest spring. It consists of a deep pool, about 7.5 m (25 feet) in diameter, which emerges directly from the subsurface.

Table 1. Rocks that comprise the Thermopolis hydrothermal system, including descriptions of lithology, hydrogeology (Hinckley et al., 1982a), and petroleum systems (De Bruin et al., 2004). Locations of oil and gas fields are depicted in Figure 2.

| Formation	Geologic Period	Thickness (meters)	Physical Description	Water Bearing Characteristics	Regional Fields Producing Oil and Gas	Regional Fields with Significant Production of Hydrogen Sulfide
Chugwater Formation	Triassic	305-360	Siltstone, shale, and fine sandstone	Fair quantities of water yields from sandstone beds. Little or no water supply otherwise	None	None
Dinwoody Formation	Triassic	12-24	Siltstone and dolomitic beds	Little or no quantities of water supply	None	None
Phosphoria Formation	Permian	60-85	Limestone and dolomite, with some siltstone and shale	Good quantities of water supply from fractured zones	Black Mountain, Lake Creek, Gebo, Hamilton Dome, Golden Eagle, Grass Creek	Black Mountain, Lake Creek
Tensleep Sandstone	Pennsylvanian	85-120	Sandstone with some dolomitic beds	Sandstone, with some dolomitic beds	Black Mountain, Lake Creek, Murphy Dome, Gebo, Hamilton Dome, Golden Eagle, Grass Creek	Black Mountain, Lake Creek
Amsden Formation	Pennsylvanian	75-100	Shale, dolomite, local basal sandstone	-	Black Mountain, Hamilton Dome, Grass Creek	Black Mountain
Madison Limestone	Mississippian	100-150	Limestone and dolomitic limestone	Excellent water quantities locally due to solution permeability, commonly under artesian pressure	Black Mountain, Hamilton Dome, Grass Creek	Black Mountain
Bighorn Dolomite	Ordovician	25-75	Massive dolomite	Same as Madison Limestone	Hamilton Dome	None
Gallatin Formation	Cambrian	135-145	Interbedded limestone, siltstone, and silty shale	Lithology suggests poor quantities of water supply	None	None
Gros Ventre Formation	Cambrian	110-155	Shale with some sandstone and limestone beds	Lithology suggests poor quantities of water supply	None	None
Flathead Sandstone	Cambrian	60-75	Sandstone, conglomeratic arkose at base	Assumed to be good quantities of water supply	None	None
Basement	Pre-Cambrian		Granite, gneiss, schist	Water only from weathered and/or fractured zones	None	None
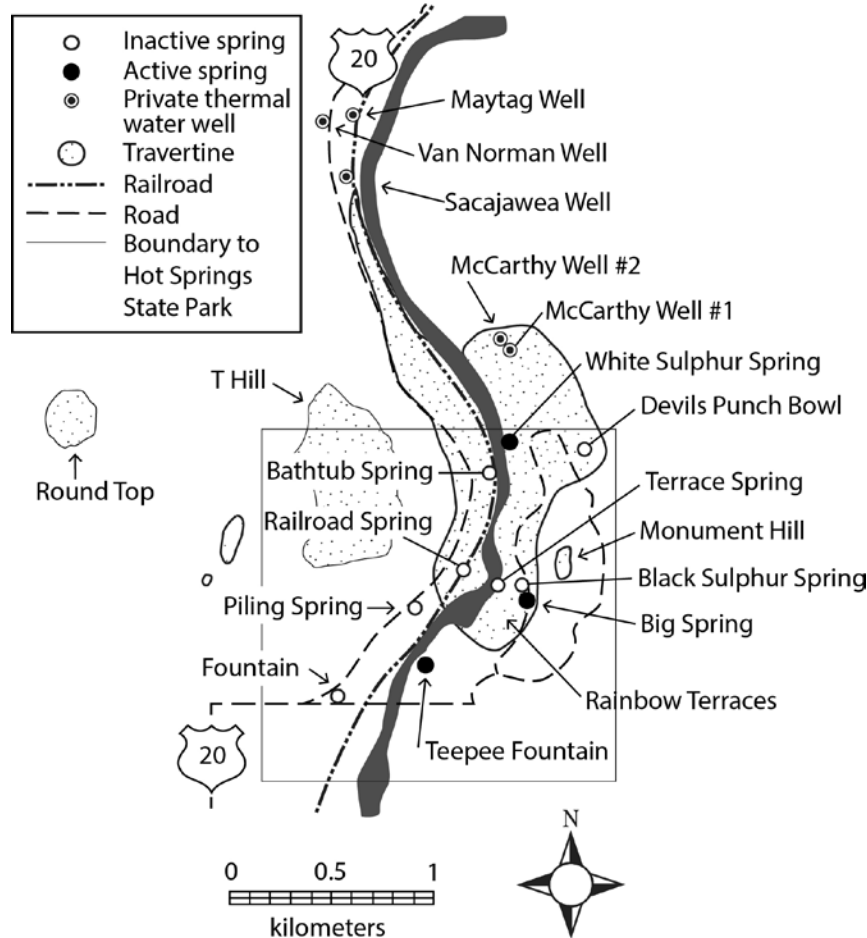
Figure 3. Locations of hot springs, travertine, and privately-owned thermal wells in the Thermopolis hydrothermal system. Hot Springs State Park is located entirely within the town of Thermopolis. Modified from Breckenridge and Hinckley (1978).

Big Spring may be deeper than 40 m (130 feet) (S. M. Smaglik, personal communication, 2010). Gas bubbles rich in CO_2 are continuously rising from the bottom of the spring. Water from the spring is funneled through a man-made channel to a series of holding pools. The thermal water is then diverted to flow over a series of travertine terraces—the Rainbow Terraces (Fig. 3)— and eventually into the Bighorn River. Big Spring has the greatest discharge of all the hot springs, roughly 1,500 gallons per minute (gpm) (Jarvis, 1986). About 400 gpm used to be diverted to flow over the Rainbow Terraces.

Big Spring feeds two large underground pipes that channel water to Teepee Fountain, the unnamed spring at the entrance to Hot Springs State Park, one public bathhouse, and two commercial establishments within the park. Thermal water from Big Spring is supplied to Teepee Fountain in the summer and fall; the fountain is not active in the winter and early spring. Teepee Fountain was constructed in 1906 by piping thermal waters through a vertical pipe. Thermal water exits the pipe at the top and runs down the sides, precipitating travertine until reaching a trough at the bottom where the water then flows through another man-made channel into the Bighorn River. Travertine has precipitated over the years to form the cone-like structure seen today. Teepee Fountain is more than 7.5 m (25 feet) in diameter and grows in diameter by about 5 to 8 cm (2 to 3 inches) each year (K. Skates, personal communication, 2010).

Travertine of the Rainbow Terraces is approximately 12 m (40 feet) thick. Water discharged from Black Sulphur Spring once flowed over the Rainbow Terraces (Burk, 1952), but this spring is no longer active. Local residents claim that Black Sulphur Spring ceased flowing after the Hebgen Lake, Montana, earthquake in 1959 (Breckenridge and Hinckley, 1978). Burk (1952) noted, however, that Black Sulphur Spring was already "slow moving" and that discharge had already been declining by 1952.

White Sulphur Spring emerges from a narrow cavity less than a foot wide at the base of travertine that is approximately 12 m (40 feet) thick. This hot spring is located approximately 1 m (several feet) above the level of the Bighorn River; the spring is no more than 0.3 m (1 foot) wide and a 6 to 8 cm (a few inches) deep and flows about 9 m (30 feet) until discharging into the river. White Sulphur Spring has a discharge of roughly 200 gpm (Jarvis, 1986). Native sulfur exists in small, localized patches on the surface of the travertine surrounding White Sulphur Spring. Sulfur deposits occur elsewhere along

the anticline within the Phosphoria Formation and were once economically mined (Woodruff, 1909).

Regional Hydrogeology and Groundwater Flow

Models for the regional hydrogeology and the source of water for the Thermopolis hydrothermal system propose the Owl Creek Mountains as the recharge zone (Hinckley et al., 1982a; Jarvis, 1986; Spencer, 1986; Paylor et al., 1989; Huntoon, 1993). Groundwater flows northward in Paleozoic aquifers, down the unnamed syncline, and up the Thermopolis Anticline, where it breaches the surface (Fig. 2). Potential contributions from recharge zones to the northeast and northwest have not been evaluated. Two models have been proposed for how groundwater flows within the Thermopolis Anticline. In one, the thrust fault that cores the Thermopolis Anticline diverts groundwater to the west-northwest, parallel to the fault (Fig. 2). At the terminus of the fault, groundwater in the Paleozoic aquifers mixes and changes flow direction to east-southeast, exploiting the higher permeability of the fractured crest of the anticline (Hinckley et al., 1982a; Jarvis, 1986; Spencer, 1986; Huntoon, 1993). An alternate model emphasizes the influence of faults that segment the anticline into blocks and domes (Paylor et al., 1989). Deep basement-controlled faults provide vertical groundwater flow paths through the anticline. Travertine deposits occur near the Owl Creek Fault (Fig. 2), for example, suggesting that thermal waters exploited the fault and flowed vertically to the surface.

Thermal modeling is consistent with the latter hydrogeologic model and attributes the heating mechanism for the Thermopolis hydrothermal system to simple conductive heating (Hinckley et al., 1982b). No evidence for heating by igneous activity has been identified. One analysis of helium isotopes (R/R_A = 0.062) (Welhan et al., 1988) suggests the thermal waters of the Thermopolis hydrothermal system do not have a mantle signature, an observation consistent with the regional model of Newell et al. (2005).

Drawdown of the Park City-Tensleep Aquifer coincides with several oil and gas fields located to the north and northwest of the Thermopolis hydrothermal system, notably Hamilton Dome, King Dome, Little Sand Draw, and Gebo (Fig. 2). A groundwater model developed for Hamilton Dome suggests that withdrawal of deep formation waters in this field has a small effect on the Thermopolis hydrothermal system (Spencer 1986).

METHODS

Oil and gas development in the southern Bighorn Basin (Fig. 2) provides a wealth of subsurface data, including gas analyses, water analyses, core samples, well logs, and bottomhole temperatures. To develop a regional geochemical perspective, analyses of formation waters sampled from the Chugwater Formation and underlying formations (Table 1) were compiled for oil and gas fields proximate to the Thermopolis hydrothermal system (Hinckley et al., 1982a, b; Wyoming Oil and Gas Conservation Commission, 2011). The quality of these data was evaluated using charge and mass balance criteria. Samples exceeding ±10% charge or mass balance were excluded from consideration. Geochemical analyses of the thermal waters of the Thermopolis hydrothermal system were first published in 1906 and most recently in 1976 (Breckenridge and Hinckley, 1978; Hinckley et al., 1982a, b). These data have been compiled and the quality evaluated using charge and mass balance criteria; no samples were excluded from consideration.

Our new geochemical data consists of water samples collected from Big Spring, White Sulphur Spring, and Teepee Fountain between June 2011 and June 2012. Big Spring and White Sulphur Spring were sampled: 1) in each of the four seasons, 2) in two sequential summer months (June and July 2010), and 3) in three sequential months in late fall and early winter (October, November, and December 2010). Teepee Fountain was sampled in fall 2010 and summer 2011. A detailed description of sampling and analysis methods is provided in Appendix A.

RESULTS

Regional Hydrogeochemistry

A total of 60 analyses of waters sampled from formations underlying the Chugwater Formation are compiled in Table 2. To provide a visual display of the data we plot select analyses from Table 2 on a Piper

diagram (Fig. 4). The one analysis of formation water of the Amsden and Park City Formations listed in Table 2 is plotted on the Piper diagram. Average compositions of formation waters of the Madison Limestone, Tensleep Sandstone, and Phosphoria Formation are also plotted. Waters of the Phosphoria Formation are separated into two groups on the diagram: waters containing high total dissolved solids (TDS) (>15,000 mg/kg) obtained from fields located to the far eastern side of Figure 2 (Zimmerman Butte, Kirby Creek, and Lake Creek) and lower TDS waters (<10,000 mg/kg) obtained from other fields. Analyses in Table 2 that are attributed to two or more formations indicate that the water could have originated from one or more of these formations or that a mixture of water from all of these formations was analyzed. We do not plot these analyses in Figure 4 because we cannot attribute them to specific formations. The significance of Figure 4 is examined in the Discussion section below.

Hydrogeochemistry of the Thermopolis Hydrothermal System

Historic Analyses

Published geochemical analyses of the thermal waters are presented in Table 3. One recorded analysis of aqueous hydrogen sulfide is reported in June 1933 (Breckenridge and Hinckley, 1978) for Big Spring (4.5 mg/L), White Sulphur Spring (2.3 mg/L), and Black Sulphur Spring (1.4 mg/L). The aqueous geochemistry of the thermal waters from all
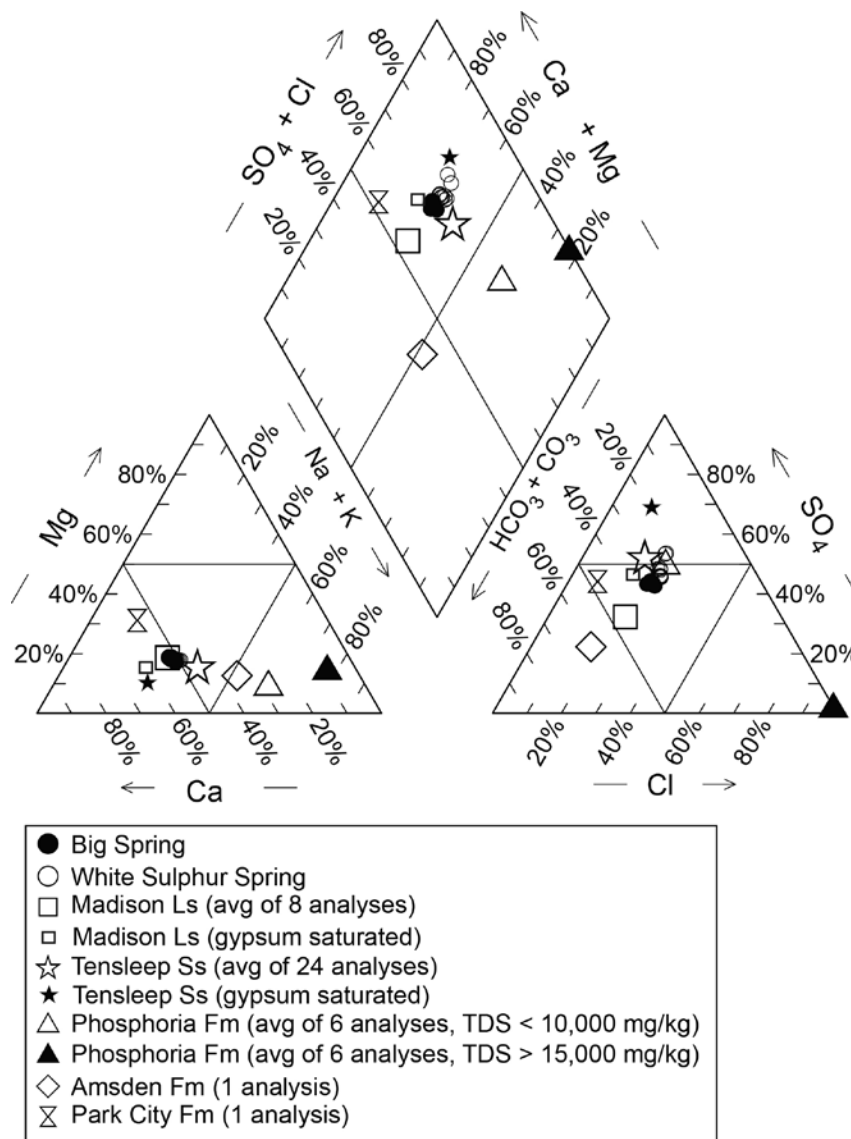
Figure 4. Piper diagram of waters from Thermopolis hydrothermal system (Big Spring and White Sulphur Spring). Also plotted are formation waters of important water-bearing formations proximate to the hydrothermal system, as determined from produced waters of regional oil and gas fields. Formation waters of the Amsden and Park City Formations, each representing one analysis, are plotted, as are average compositions of formation waters of the Madison Limestone, Tensleep Sandstone, and Phosphoria Formation. Waters of the Phosphoria Formation are separated into two groups: high TDS waters (>15,000 mg/kg) obtained from fields on the far eastern side of Figure 2 (Zimmerman Butte, Kirby Creek, and Lake Creek) and lower TDS waters (<10,000 mg/kg) obtained from other fields. Chemical analyses and their sources are supplied in Table 2 (formation waters) and Table 4 (waters from the hydrothermal system).

of these hot springs is broadly similar, with a few exceptions. Sodium, chloride, and sulfate concentrations are comparatively low for the waters analyzed in 1906, whereas potassium and magnesium concentrations are comparatively high for the waters

Table 2. Aqueous geochemistry of formation waters sampled from oil and gas fields proximate to the Thermopolis hydrothermal system. Locations of the fields are depicted in Figure 2. Data compiled from Hinckley et al. (1982a) (data noted with asterisk) and Wyoming Oil and Gas Conservation Commission (2011). A list of two or more formations indicates that the water being analyzed could have originated from one or more of these formations, or that a mixture of water from these formations was analyzed. Concentrations in mmol/L unless otherwise specified.

Formation	Oil and Gas Field	Location	Well	API#	Sampling Date	Temp (C)	pH	SiO_2	Na	K	Mg	Ca	Fe	Cl	HCO_3	SO_4	TDS (mg/L)	Charge Balance (%)
Park City*	-	T42N R95W Sec 25	-	-	-	22	8	0.46	1.8	0.2	2.1	3.6	0.018	1.1	6.2	2.9	-	1.1%
Phosphoria	Waugh	SW NE Sec 12 T 44 N R 97 W	12-1 FEDERAL	049-017-20238	09 16 08	-	7	-	14.2	-	2.8	9.6	-	11.3	1.2	13.3	2538	-0.1%
Phosphoria	Kirby Creek	NW SE Sec 17 T 43 N R 92 W	1 KIRBY CREEK UNIT	049-017-05333	03 15 75	-	8.6	-	551.2	7.4	4.9	16.2	-	321.6	37.0	117.1	37744	0.7%
Phosphoria	Kirby Creek	SW NE Sec 17 T 43 N R 92 W	9 UNIT B-041616	049-017-20679	08 22 84	-	7.8	-	340.3	15.3	64.6	51.6	-	420.3	26.4	70.8	34557	0.0%
Phosphoria	Kirby Creek	SE NW Sec 17 T 43 N R 92 W	10 UNIT	049-017-20688	08 20 84	-	7	-	566.7	7.2	95.4	4.1	-	631.9	33.0	54.1	44385	0.0%
Phosphoria	Kirby Creek	NE NE Sec 21 T 43 N R 92 W	3 KIRBY CREEK OPC	049-017-05309	07 15 82	-	7.7	-	52.2	0.4	0.5	2.2	-	19.2	9.7	14.6	3688	0.0%
Phosphoria	Kirby Creek	NE SW Sec 22 T 43 N R 92 W	3 KYNE UNIT PAT.	049-017-05272	07 14 82	-	7.7	-	52.2	0.4	0.5	2.2	-	19.2	9.7	14.6	3688	0.0%
Phosphoria	Kirby Creek	SW SE Sec 17 T 43 N R 92 W	13 UNIT B-041616	049-017-20686	08 9 04	-	7.72	-	183.6	2.3	1.9	15.7	-	88.9	20.6	61.0	15100	-2.3%
Phosphoria	Little Sand Draw	SE NW Sec 2 T 44 N R 96 W	14 NELSON	049-017-20407	08 21 91	-	6.9	-	10.7	1.1	3.2	13.4	-	4.3	10.2	17.5	3050	-4.6%
Phosphoria	King Dome	NW SW Sec 19 T 44 N R 96 W	6 OGLE FEDERAL	049-017-20857	02 2 91	-	7.2	-	11.0	1.6	5.0	10.1	-	7.6	13.9	8.1	2290	3.9%
Phosphoria	Hamilton Dome	SE NW Sec 14 T 44 N R 98 W	93 PLACER C-044140	049-017-07232	06 23 97	-	7.2	-	49.3	-	2.1	13.0	-	28.2	13.3	21.9	5687	0.0%
Phosphoria	Grass Creek	NE NW Sec 18 T 46 N R 98 W	44H EHRLICH	049-017-20796	12 4 85	-	6.7	-	64.6	1.8	1.3	7.0	0.00090	16.8	46.1	12.9	2820	-2.4%
Embar	Gebo	SE SE Sec 15 T 44 N R 95 W	62 GEBO UNIT	049-017-20152	11 19 82	-	7.68	-	13.2	1.6	1.3	13.2	-	2.6	8.0	17.9	2977	-2.9%
Embar	Hamilton Dome	SE NE Sec 14 T 44 N R 98 W	19-14 WIW CURTIS	049-017-05737	07 27 65	-	8.2	-	22.1	4.5	3.7	11.6	-	12.1	20.6	12.5	3496	-0.5%
Tensleep	Waugh	SE NE Sec 12 T 44 N R 97 W	1 BIGGS GOVT	049-017-05879	10 21 08	-	6.8	-	6.7	-	1.9	8.1	1.2	9.0	1.3	8.2	1787	4.2%
Tensleep	Golden Eagle	NE SW Sec 12 T 45 N R 97 W	12 GOLDEN EAGLE UNIT	049-017-20868	07 14 09	-	6.3	-	22.4	2.6	3.2	9.4	-	4.7	19.5	11.7	2976	2.7%
Tensleep	Golden Eagle	NE SW Sec 12 T 45 N R 97 W	12 GOLDEN EAGLE UNIT	049-017-20868	05 18 10	-	6.56	-	44.1	0.6	2.0	9.4	-	8.5	20.6	19.2	4231	0.0%
Tensleep	Golden Eagle	NE SW Sec 12 T 45 N R 97 W	12 GOLDEN EAGLE UNIT	049-017-20868	07 14 09	-	6.3	-	22.4	2.6	3.2	9.4	-	4.7	19.5	11.7	2976	2.7%
Tensleep	Golden Eagle	NE SW Sec 12 T 45 N R 97 W	12 GOLDEN EAGLE UNIT	049-017-20868	05 18 10	-	6.56	-	44.1	0.6	2.0	9.4	-	8.5	20.6	19.2	4231	0.0%
Tensleep	Zimmerman Butte	NE SE Sec 35 T 44 N R 93 W	9-35 HUSKY C-068430	049-017-20528	01 21 83	-	7	-	1.3	0.6	1.0	5.6	-	7.6	4.2	2.6	986	1.6%
Tensleep	Lake Creek	NE NW Sec 34 T 43 N R 91 W	12 UNIT B-016999	049-017-05203	03 29 09	-	-	-	5.7	0.1	1.0	4.3	0.0020	0.3	6.6	4.6	975	1.6%
Tensleep	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	08 10 75	-	7.5	-	10.0	0.3	3.3	8.7	-	1.6	3.6	14.6	2235	0.0%
Tensleep	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	08 29 75	-	7.2	-	4.2	0.2	1.8	8.6	-	0.9	1.2	12.0	1730	-2.0%
Tensleep	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	09 2 75	-	7.4	-	3.3	0.2	3.0	8.0	-	1.0	2.8	10.9	1647	-0.1%
Tensleep	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	09 5 75	-	7.7	-	3.3	0.3	4.1	7.4	-	1.0	2.8	11.4	1702	-0.1%
Tensleep	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	09 15 75	-	6.8	-	1.3	0.4	1.3	4.5	-	0.6	7.8	2.4	739	0.0%
Tensleep	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	09 22 75	-	6.8	-	2.7	0.5	2.3	3.9	-	1.2	9.0	2.7	869	0.1%
Tensleep	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	10 8 75	-	6.8	-	1.5	0.5	2.3	3.5	-	0.8	7.8	2.5	754	0.1%
Tensleep	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	07 14 76	-	8.1	-	6.0	0.6	2.4	3.8	-	1.9	9.6	2.5	1042	6.8%
Tensleep	Black Mountain	SE SW Sec 31 T 43 N R 90 W	17 UNIT B-036791	049-043-05021	1961 (?)	-	8.3	-	4.0	-	0.9	0.5	-	0.7	5.5	0.1	384	2.9%
Tensleep	Black Mountain	NE NW Sec 36 T 43 N R 91 W	8 BLACK MOUNTAIN UNIT	049-017-07278	06 17 61	-	7.8	-	4.3	-	1.0	1.5	-	0.6	6.6	1.0	397	0.0%
Tensleep	Black Mountain	NE NW Sec 36 T 43 N R 91 W	8 BLACK MOUNTAIN UNIT	049-017-07278	11 8 62	-	7.3	-	1.0	-	1.0	1.6	-	0.4	5.8	0.2	324	0.1%
Tensleep	Black Mountain	SW NE Sec 36 T 43 N R 91 W	53 BLK MT UNIT WY-3096	049-017-20221	06 17 61	-	7.7	-	3.6	-	1.5	2.0	-	2.8	6.2	0.8	750	-0.5%
Tensleep	Hamilton Dome	NE NW Sec 24 T 44 N R 98 W	3 PLACER	049-017-05580	01 22 83	-	8	-	46.6	4.8	3.5	15.0	-	26.5	29.0	16.4	5334	0.0%
Tensleep	Hamilton Dome	NE NE Sec 23 T 44 N R 98 W	43 RATHVON C-058729	049-017-05568	06 20 84	-	7.4	-	36.6	2.7	3.7	14.0	-	23.4	18.4	16.4	4561	0.0%
Tensleep	Hamilton Dome	NW NE Sec 24 T 44 N R 98 W	123 PLACER	049-017-20450	03 7 05	-	6.88	-	19.7	2.8	4.3	16.4	0.018	12.3	23.8	13.9	4545	0.0%
Tensleep	Hamilton Dome	NE NW Sec 24 T 44 N R 98 W	3 PLACER WIW	049-017-20630	01 22 83	-	8	-	46.6	4.8	3.5	15.0	-	26.5	29.0	16.4	5334	0.0%
Tensleep	Hamilton Dome	SW NE Sec 14 T 44 N R 98 W	109 PLACER CHY C-44140	049-017-20276	12 16 97	-	7.91	-	0.3	2.5	4.5	15.8	0.045	18.3	6.7	9.3	2816	-0.2%
Tensleep	Gebo	NE SE Sec 23 T 44 N R 95 W	5 GEBO UNIT	049-017-05483	08 13 82	-	7.86	-	26.4	1.9	2.7	10.8	-	11.6	10.4	22.2	4034	-9.0%
Tensleep*		T42N R95W Sec 13		-	-	19.5	7.8	0.46	4.9	0.6	3.5	7.0	-	3.5	11.7	5.6	-	-0.1%
Amsden	Hamilton Dome	SW SW Sec 13 T 41 N R 98 W	46BA PLACER	049-017-05626	03 13 06	-	6.87	-	20.1	1.3	2.4	6.9	0.0018	7.0	24.2	4.5	3009	-0.2%

Table 2 (continued).

Formation	Field	Location	Well name	Number	Date		pH										TDS	
Madison	Golden Eagle	NE SW Sec 12 T 45 N R 97 W	12 GOLDEN EAGLE UNIT	049-017-20868	04 27 11	–	7	–	7.8	–	3.9	8.0	–	8.5	19.0	2.3	2274	-0.6%
Madison	Golden Eagle	NE SW Sec 12 T 45 N R 97 W	12 GOLDEN EAGLE UNIT	049-017-20868	04 27 11	–	7	–	7.8	–	3.9	8.0	–	8.5	19.0	2.3	2274	-0.6%
Madison	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	07 29 75	–	7.3	–	14.3	1.3	3.9	11.4	–	8.5	19.0	9.4	2703	0.0%
Madison	Red Springs	SW SW Sec 21 T 43 N R 93 W	W-2 BROWN-GOV'T	049-017-07296	07 25 75	–	7.4	–	13.0	1.3	3.9	11.3	–	8.2	18.8	8.8	2603	0.0%
Madison	Hamilton Dome	NW NW Sec 24 T 44 N R 98 W	6M RATHVON	049-017-05552	01 6 83	–	7.9	–	14.0	2.1	3.5	10.0	–	9.8	18.2	7.5	2509	0.0%
Madison	Hamilton Dome	NW SE Sec 14 T 44 N R 98 W	114 PLACER	049-017-20359	02 5 80	–	6.3	–	15.0	1.3	2.6	9.4	–	10.2	19.4	5.4	2295	0.0%
Madison	Hamilton Dome	NW NW Sec 14 T 44 N R 98 W	6 FEDERAL 044177	049-017-05813	01 6 83	–	7.9	–	14.0	2.1	3.5	10.0	–	9.8	18.2	7.5	2509	0.0%
Madison	Hamilton Dome	NW SE Sec 14 T 44 N R 98 W	45 WIW W-044141	049-017-05689	08 27 08	–	6.76	–	3.1	1.6	3.6	14.1	–	8.7	15.1	8.5	2854	-0.9%
Phosphoria-Tensleep	Golden Eagle	NE SW Sec 12 T 45 N R 97 W	2 GOLDEN EAGLE UNIT	049-017-05960	07 14 09	–	6.55	–	26.8	3.1	3.5	10.7	–	8.2	25.1	10.2	3294	4.2%
Phosphoria-Tensleep	Golden Eagle	NE SW Sec 12 T 45 N R 97 W	2 GOLDEN EAGLE UNIT	049-017-05960	07 14 09	–	6.55	–	26.8	3.1	3.5	10.7	–	8.2	25.1	10.2	3294	4.2%
Phosphoria-Tensleep	Golden Eagle	NE SW Sec 12 T 45 N R 97 W	2 GOLDEN EAGLE UNIT	049-017-05960	05 18 10	–	7.39	–	47.8	0.7	1.1	10.3	–	14.1	24.8	16.2	4368	0.0%
Phosphoria-Tensleep	Little Sand Draw	NE NW Sec 2 T 44 N R 96 W	28 NELSON C-068665	049-017-20507	08 21 91	–	7.4	–	9.9	1.3	3.0	12.0	–	4.5	8.1	13.6	2550	1.5%
Phosphoria-Tensleep	King Dome	SE SW Sec 19 T 44 N R 96 W	3 OGLE FEDERAL	049-017-20504	03 15 91	–	7.3	–	14.1	2.9	4.5	12.0	–	8.4	16.1	11.7	2930	2.1%
Phosphoria-Tensleep	Hamilton Dome	NW SW Sec 13 T 44 N R 98 W	76 PLACER	049-017-05673	03 21 96	–	6.85	–	37.7	–	11.1	10.0	–	21.2	12.1	23.3	4900	0.0%
Embar-Tensleep	Black Mountain	NE NE Sec 35 T 43 N R 91 W	57 BLACK MOUNTAIN UNIT	049-017-20677	–	–	7.61	–	14.0	0.1	0.5	14.4	–	1.2	6.7	18.5	3090	-1.1%
Embar-Tensleep	Gebo	SW NE Sec 23 T 44 N R 95 W	52 W-066743	049-017-20099	11/4/1881	–	2.7	–	13.5	1.0	2.6	9.9	–	6.2	7.6	12.7	2479	0.5%
Phos-Tensl-Darwin-Mad	Hamilton Dome	SE NW Sec 13 T 44 N R 98 W	100 PLACER CHY C-044140	049-017-20258	03 7 05	–	7.25	–	19.7	2.8	4.3	16.4	0.018	12.3	23.8	13.9	4545	0.0%
Phosph-Tensl-Mad	Hamilton Dome	NW SE Sec 14 T 44 N R 98 W	85 PLACER C-044140	049-017-05668	05 8 99	–	6.2	–	17.3	1.8	3.4	11.1	0.011	8.9	20.0	9.6	3457	-0.1%
Amsden-Madison	Hamilton Dome	SW SW Sec 13 T 44 N R 98 W	131 PLACER/RATHVON	049-017-20935	11 16 07	–	7.66	–	30.1	1.4	2.8	8.3	0.013	23.0	16.5	7.3	3674	-0.2%

analyzed in 1906 and 1926. The large positive charge imbalance calculated for Big Spring water analyzed in 1906 and 1926 is because bicarbonate was not measured. For the rest of the analyses, combined concentrations of calcium, magnesium, and bicarbonate exceed 50% of total dissolved constituents, whereas no specific cation-anion pair exceeds 50% of this total.

This Study

Results of field measurements, laboratory analyses, and geochemical calculations generated in this study for Big Spring, White Sulphur Spring, and Teepee Fountain are presented in Table 4. The composition of the three springs is fairly uniform; the concentration of all ions among the three springs does not vary more than analytical uncertainty over the course of a year of sampling. This uniformity persists through the seasons, in consecutive months and days, and at different times of the day. The only notable exception to this uniformity is for calcium and magnesium in Big Spring between November and December 2010 and again between December 2010 and April 2011. Calcium concentration decreased by 0.37 mmol/kg (-5%; analytical uncertainty of 0.06 mmol/kg) between November and December and subsequently increased by 0.72 mmol/kg (+10%; analytical uncertainty of 0.07 mmol/kg) between December and April. Magnesium concentration decreased by 0.34 mmol/kg (-12%; analytical uncertainty of 0.03 mmol/kg) between November and

Table 3. Historic geochemical analyses of the Thermopolis hydrothermal system. Concentrations in mmol/L unless otherwise specified. Locations of springs and wells, except Spomer, are depicted in Figure 4. Tabulated from Breckenridge and Hinckley (1978).

Spring or Well	Sampling Date	TDS (mg/L)	Conductivity (micromhos)	T°C	pH	Ca	Mg	Fe	Na	K	SiO_2(aq)	Cl	F	HCO_3	NO_3	SO_4	Charge Balance Error (%)
Sacajawea	4/21/1969	-	3170	-	6.6	9.9	3.1	-	9.9	1.2	-	8.5	-	12.1	0.002	8.5	-0.8
Sacajawea	9/2/1976	2390	3140	52	7.0	8.5	3.2	0	11.7	1.0	1.2	8.5	0.28	12.5	0	8.7	-3.4
McCarthy	9/3/1976	2380	3120	54	7.1	8.7	3.1	-	11.7	1.0	1.3	8.5	0.23	12.5	0	8.6	-2.6
Spomer	2/20/1981	-	-	49	6.6	8.5	2.7	-	11.7	0.9	1.2	10.2	0.24	10.2	0.0016	7.9	-1.9
White Sulphur	6/12/1933	2321	3090	-	-	9.6	3.3	0.02	11.0	1.2	1.3	8.7	0.20	12.8	0.0016	8.0	0.2
White Sulphur	9/2/1976	2350	2990	53	7.0	8.5	3.2	0.001	11.7	1.1	1.3	8.5	0.43	12.3	0	8.5	-2.9
Bathtub	9/3/1976	2330	3090	53	7.1	8.5	3.0	-	11.7	1.1	1.4	9.3	0.22	12.0	0	8.1	-2.6
Black Sulphur	6/12/1933	2378	2990	55	-	9.6	3.1	0.001	11.6	1.3	2.5	9.4	0.20	12.1	0.0016	8.1	0.4
Big Spring	1906	-	-	-	-	7.9	4.6	-	3.6	2.3	1.4	2.4	-	-	0	5.8	37.7
Big Spring	1926	-	-	-	-	7.9	4.6	-	11.2	2.3	1.4	10.0	-	-	-	5.8	28.1
Big Spring	6/22/1933	2373	-	-	-	9.6	3.1	0.001	11.4	1.3	1.4	9.3	0.19	12.6	-	8.0	0.2
Big Spring	4/11/1958	2280	3150	-	6.4	9.5	2.8	0.001	12.2	1.4	1.4	8.9	0.16	12.1	0.0016	8.1	0.9
Big Spring	2/24/1971	2200	2860	-	7.0	9.0	3.5	0.001	10.9	1.3	1.2	8.3	0.29	11.6	0	8.1	1.2
Big Spring	9/2/1976	2190	2960	56	6.9	7.7	2.9	0	10.9	0.95	1.3	8.5	0.36	11.6	0	7.6	-3.7

December and subsequently increased by 0.39 mmol/kg (+16%; analytical uncertainty of 0.01 mmol/kg) between December and April. Sulfate and chloride concentrations do not display comparable differences, and the alkalinity of the springs was calculated from the chemical analysis by charge difference for the November and December sampling events. We, therefore, lack sufficient data to provide plausible explanations for these differences.

Combined concentrations of calcium, magnesium, and bicarbonate exceed 50% of the total dissolved constituents, and no specific cation-anion pair exceeds 50% of the total. All three springs emit the characteristic odor of hydrogen sulfide gas. Of the three springs, Big Spring exhibits the highest temperature (52.5–53.0°C), the lowest pH (6.2–6.4), and the lowest amount of dissolved oxygen (0.1–0.5 mg/L). Temperatures are progressively cooler in White Sulphur Spring (47.3–48.2 °C) and Teepee Fountain (36.1–41.0 °C), whereas pH (White Sulphur Spring, 6.3–6.5; Teepee Fountain, 7.7–7.8) and dissolved oxygen (White Sulphur Spring, 1.1–2.5 mg/L; Teepee Fountain, 3.7–5.7 mg/L) are progressively higher. Conductivity (2,526–4,352 µS/cm) and specific conductance (1,431–4,258 µS/cm) is similar in each of the three springs.

Thermal waters in all three springs are variably saturated with respect to the carbonate minerals aragonite (SI = -0.15 to 1.3) and calcite (SI = -0.01

Table 4. Aqueous geochemistry of hot springs, Thermopolis hydrothermal system (this study). Concentrations in mmol/kg unless otherwise specified.

The last seven columns (Calcite, Aragonite, Dolomite, Gypsum, Anhydrite, Barite, Quartz) are **Saturation Indices**.

Sampling Date	T (°C)	pH	DO (mg/L)	Pressure (atm)	SPC (mS/cm)	C (mS/cm)	ORP (mV)	Ca	Mg	Na	K	SiO_2	Cl	HCO_3	HCO_3 by difference	SO_4	Al (µmol/kg)	Fe (µmol/kg)	Mn (µmol/kg)	Ba (µmol/kg)	Charge Balance (%)	log PCO_2	DIC (mmol/kg)	Calcite	Aragonite	Dolomite	Gypsum	Anhydrite	Barite	Quartz
Big Spring																														
06 6 10	52.5	6.22	0.2	0.81	2032	3101	-261.7	7.76	2.76	9.00	0.98	0.59	6.81	---	12.2	5.92	0.01	<0.06	0.38	0.30	---	-0.22	24.13	0.28	0.13	1.32	-0.67	-0.58	0.09	0.34
07 23 10	52.9	6.29		0.86	2573	3933	-202.2	7.64	2.80	8.80	0.97	0.59	6.83	---	11.8	5.89	0.03	<0.06	0.38	0.29	---	-0.30	21.87	0.34	0.19	1.45	-0.67	-0.59	0.07	0.33
10 1 10	52.7	6.15	0.2	0.86	2566	3918	-208.1	7.66	2.75	8.75	0.91	0.57	6.84	---	11.5	5.96	0.06	<0.06	0.40	0.28	---	-0.17	24.73	0.18	0.04	1.13	-0.66	-0.58	0.07	0.32
10 2 10	52.6	6.19	0.2	0.86	2568	3925	-244.8	7.43	2.67	8.39	0.88	0.56	6.77	---	10.7	5.91	0.03	<0.06	0.40	0.28	---	-0.24	21.92	0.18	0.04	1.13	-0.67	-0.59	0.07	0.31
11 13 10	52.7	6.20	0.2	0.86	2534	3865	-179.8	7.62	2.76	8.43	0.90	0.57	7.05	---	11.2	5.84	0.02	<0.06	0.38	0.28	---	-0.23	22.67	0.22	0.08	1.21	-0.67	-0.59	0.07	0.32
11 14 10	52.5	6.28	0.2	0.86			-276.3	7.47	2.71	8.25	0.91	0.56	6.87	---	10.7	5.86	0.06	<0.06	0.38	0.28	---	-0.33	19.99	0.27	0.13	1.32	-0.67	-0.59	0.07	0.31
12 10 10	52.7	6.20	0.5	0.85	3888	2541	-243.2	7.10	2.37	8.81	0.95	0.52	6.73	---	10.0	5.91	0.10	<0.06	0.36	0.27	---	-0.28	20.18	0.15	0.00	1.02	-0.68	-0.59	0.07	0.28
12 11 10	52.8	6.29	0.5	0.86	3866	2526	-243.2	7.17	2.36	8.85	0.93	0.53	6.69	---	10.2	5.87	0.13	<0.06	0.35	0.27	---	-0.36	18.85	0.25	0.11	1.23	-0.68	-0.59	0.07	0.29
04 15 11	52.7	6.25	0.1	0.85	2619	4007	-235.2	7.89	2.75	9.12	0.91	0.53	6.25	8.52	13.1	5.89	0.10	<0.16	0.29	0.28	9.2	-0.40	16.41	0.18	0.03	1.11	-0.65	-0.56	0.06	0.29
04 16 11	52.6	6.29	0.1	0.85	2578	3938	-224.5	7.68	2.81	8.92	0.90	0.52	6.07	8.78	13.1	5.69	0.10	<0.16	0.31	0.28	9.0	-0.43	16.25	0.22	0.08	1.22	-0.67	-0.59	0.05	0.28
06 15 11	52.5	6.35	0.1	0.85	2609	3981	-225.2	7.57	2.71	8.55	0.91	0.54	6.48	8.92	11.6	5.87	0.12	<0.20	0.35	0.27	5.5	-0.48	15.59	0.28	0.13	1.31	-0.66	-0.58	0.06	0.30
06 16 11	52.5	6.32	0.1	0.85	2619	3992		7.75	2.77	8.49	0.90	0.53	6.37	8.75	12.2	5.81	0.15	<0.20	0.35	0.28	7.2	-0.46	15.73	0.25	0.11	1.26	-0.66	-0.58	0.06	0.29
White Sulphur Spring																														
06 6 10	48.2	6.49	2	0.86	1431	2056	132.8	9.05	3.16	11.05	1.07	0.61	8.15	---	13.6	7.33	14.02	3.17	0.89	0.28	---	-0.22	24.13	0.28	0.13	1.32	-0.67	-0.58	0.09	0.34
07 24 10	48.1	6.51						9.18	3.22	11.12	1.07	0.64	8.16	---	14.2	7.21	8.29	1.00	0.75	0.29	---	-0.30	21.87	0.34	0.19	1.45	-0.67	-0.59	0.07	0.33
10 2 10	48.2	6.37	1.1	0.86	2981	4300	-201.2	9.14	3.24	11.21	1.03	0.60	8.24	---	14.1	7.23	4.87	0.75	0.67	0.25	---	-0.17	24.73	0.18	0.04	1.13	-0.66	-0.58	0.07	0.32
11 13 10	47.8	6.34	1.1	0.86	2936	4216	-229.9	9.21	3.19	10.59	0.98	0.59	8.18	---	13.6	7.20	4.74	0.57	0.66	0.25	---	-0.24	21.91	0.18	0.04	1.13	-0.67	-0.59	0.07	0.31
11 14 10	47.8	6.34	1.2	0.86	2503	3594	-235.3	9.34	3.23	10.91	1.05	0.60	8.23	---	14.3	7.19	5.66	0.63	0.66	0.25	---	-0.23	22.67	0.22	0.08	1.21	-0.67	-0.59	0.07	0.32
12 9 10	48.2	6.37	2.5	0.86	2915	2032	-241.4	8.39	3.00	11.11	1.10	0.55	8.07	---	10.7	8.03	6.12	0.41	0.60	0.23	---	-0.33	19.99	0.27	0.13	1.32	-0.68	-0.59	0.07	0.31
12 10 10	47.8	6.40	1.7	0.85	4258	2964	-236.8	8.46	3.00	10.63	1.10	0.55	8.14	---	10.5	7.90	4.31	0.48	0.58	0.24	---	-0.28	20.19	0.15	0.00	1.02	-0.68	-0.59	0.07	0.28
04 16 11	47.3	6.48	1.1	0.85	3050	4352	-205.9	8.77	3.10	11.38	1.02	0.53	7.49	8.80	13.3	7.59		0.52	0.51	0.15	7.6	-0.36	18.85	0.25	0.11	1.23	-0.65	-0.59	0.07	0.29
06 15 11	47.8	6.34	1.1	0.05	3010	4322	-197	9.15	3.25	10.09	1.07	0.57	7.52	7.27	11.1	8.58	18.89	7.75	1.06	0.25	6.3	-0.40	16.41	0.18	0.03	1.11	-0.67	-0.56	0.06	0.29
06 16 11	47.8	6.31	1.2	0.85	3025	4340	-203.5	8.71	3.01	10.74	1.05	0.57	7.59	7.57	10.2	8.65	18.67	7.29	1.00	0.24	4.3	-0.43	16.25	0.22	0.08	1.22	-0.67	-0.59	0.05	0.28
Teepee Fountain																														
10 2 10	37.0	7.82	5.4	0.86	2481	3050	-85	7.01	2.83	8.80	0.96	0.60	7.16	---	9.9	6.08	5.46	<0.06	0.24	0.23	---	-2.01	11.05	1.53	1.38	3.85	-0.71	-0.77	0.20	0.58
06 7 10	39.4	7.82	4.5	0.85	2420	3085	18	7.58	2.90	9.40	0.94	0.61	6.99	---	12.2	5.95	0.06	<0.06	0.33	0.27	---	-1.90	13.70	1.67	1.53	4.13	-0.70	-0.74	0.21	0.54
07 25 10	36.8	7.74						7.21	2.94	9.35	0.90	0.61	7.07	---	11.2	6.03	0.02	<0.06	0.25	0.25	---	-1.88	12.52	1.50	1.36	3.81	-0.71	-0.77	0.22	0.59
06 15 11	36.1	7.89	5.7	0.85	2511	3042	13.3	7.00	2.80	9.15	1.02	0.59	6.68	7.54	10.6	6.13	0.12	<0.20	0.22	0.24	6.3	-2.20	8.42	1.47	1.33	3.73	-0.69	-0.76	0.24	0.58
maximum uncertainty								0.19	0.07	0.29	0.08	0.01	0.04	5%		0.13	0.04	0.07	0.04	0.01										

to 1.5), whereas these waters are supersaturated with respect to dolomite (SI = 0.71 to 3.7). These waters are also saturated with respect to barite (SI = -0.08 to 0.24), but are undersaturated with respect to anhydrite (SI = -0.45 to -0.76). The degassed waters of Teepee Fountain are the most saturated with respect to carbonate minerals and barite; waters of White Sulphur Spring and Big Spring, respectively, are progressively less saturated with these minerals. Partial pressures of CO_2 range from $10^{-0.17}$ to $10^{-0.48}$, and concentrations of dissolved inorganic carbon range from approximately 16 to 25 mmol/kg for both Big Spring and White Sulphur Spring (Table 4).

The composition of the three springs is broadly similar to historic geochemical data published for the Thermopolis hydrothermal system (compare Tables 3 and 4). Big Spring possesses the most complete record of historic geochemical data; we plot these historic analyses as well as our results for Na, Ca, Mg, Cl, SO_4, and HCO_3 in Big Spring waters in Figure 5. Several anomalies exist in the historic data set for the aqueous geochemistry of Big Spring. These anomalies center on differences in the water chemistry reported in 1906 and 1926 relative to the water chemistry reported in 1933, 1958, 1971, 1976, and this study. No bicarbonate analyses are reported for 1906 or 1926; thus, it's difficult to evaluate the quality of the 1906 and 1926 data using charge and mass balance criteria. No known temperature data is available before 1976. Analytical uncertainties are not available
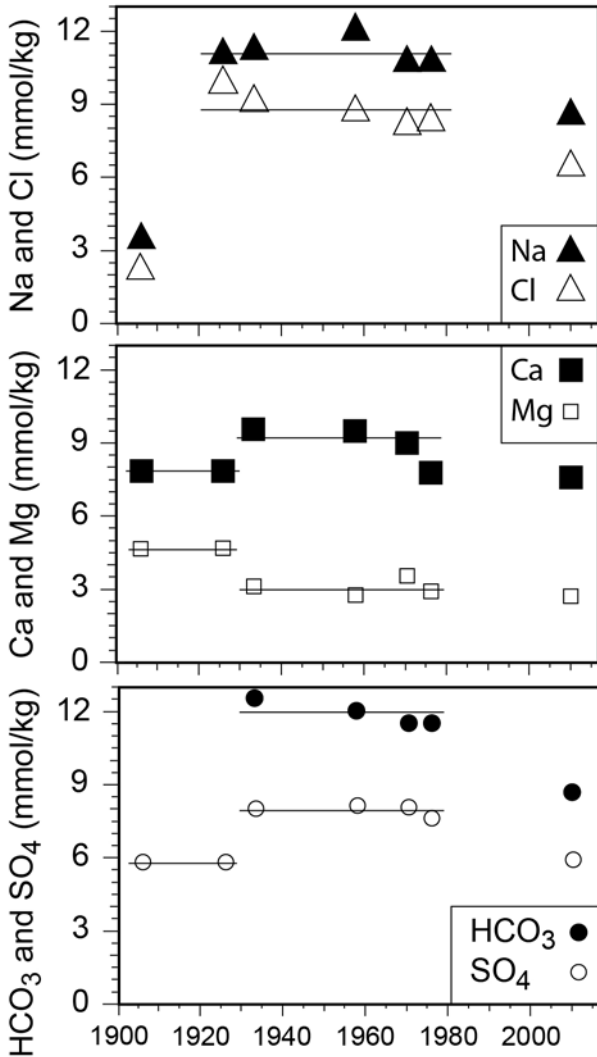
Figure 5. Water analyses for Big Spring as a function of time (data from this study and from sources listed in Table 3). Data plotted for 2010 are the mean of all analyses performed for this study. The symbols are the size of the two sigma uncertainty for the analyses determined in this study; analytical uncertainties are not available for the historic analyses. Trend lines are drawn to help guide the eye and are not statistically significant.

for any of the analyses published prior to this study, making the task of evaluating and interpreting the data set even more difficult.

Sodium and chloride concentrations reported for 1906 are about one-third lower than concentrations reported for subsequent years; these concentrations remain relatively constant between 1933 and 1976. Calcium and sulfate concentrations are consistent between 1906 and 1926, but are about one-sixth lower than subsequent calcium and sulfate analyses.

Magnesium concentrations are consistent between 1906 and 1926, but are about 50% greater than subsequent magnesium analyses. Differences in calcium, sulfate, and magnesium concentrations are small enough to be within the realm of analytical uncertainty, but are large enough to be consistent with real changes in the evolution of these ions. Between 1933 and 1976, concentrations of all of the ions remained relatively constant. In our study, magnesium concentrations are similar to those measured in 1976, whereas concentrations of HCO_3, Cl, SO_4, Na, and Ca are less than those measured in 1976.

Analyses of Big Spring and White Sulphur Spring waters determined for this study (a total 22 analyses) are plotted on the Piper diagram depicted in Figure 4. Big Spring waters plot in a tight cluster in the upper quadrant of the quadrilateral portion of the diagram; White Sulphur Spring waters plot near Big Spring waters with a slightly greater distribution.

DISCUSSION

The thermal waters of the Thermopolis hydrothermal system contain combined concentrations of calcium, magnesium, and bicarbonate that exceed 50% of the total; such waters are generally considered "hard" and characteristic of carbonate aquifers or rocks containing abundant carbonate minerals. No specific cation-anion pair exceeds 50% of the total in any of the thermal waters; this geochemical signature is generally produced by dissolution of multiple minerals or by mixing of two or more chemically distinct groundwaters (Freeze and Cherry, 1979).

Gas bubbles rich in CO_2 are continuously rising from the bottom of Big Spring, and all of the thermal waters emit the characteristic odor of hydrogen sulfide gas. No evidence for heating by igneous activity has been identified for the Thermopolis hydrothermal system (Hinckley et al., 1982a). The source of the abundant CO_2, however, has not been identified, and our results do not shed light on its origin.

In their evaluation of the Thermopolis hydrothermal system, Hinckley et al. (1982b) proposed that the thermal waters are a mixture of groundwater from Paleozoic aquifers. We use a Piper diagram to begin to assess this hypothesis; Piper diagrams provide one means of identifying and evaluating geochemical trends for evidence of mixing processes (Crossey et al., 2006; Crossey et al., 2009;

Williams et al., 2013). We compare the composition of the thermal waters of Big Spring and White Sulphur Spring with the composition of formation waters of important Paleozoic aquifers (Table 2) on the Piper diagram in Figure 4. If the thermal waters are a mixture of two end members, the compositions will lie on a straight line in each of the fields of the diagram (Drever, 1997). If the thermal waters are a mixture of three end members, the compositions will lie within an area bounded by the three. Observing these trends on Piper diagrams strongly suggests—but does not prove—mixing as a controlling process. Big Spring and White Sulphur Spring water compositions do not lie along a straight line or within an area defined by formation waters of any of the Paleozoic aquifers (Fig. 4), suggesting that the thermal waters are not a mixture of these formation waters. Analyses of formation waters, however, display a wide range of composition for the Madison Limestone, Tensleep Sandstone, and Phosphoria Formation (Table 2). For most of the analyses, the value of the standard deviation (2 σ) calculated for analyses from each of these formations is as large as the mean value. We illustrate the consequences of these uncertainties with respect to two important Paleozoic aquifers: the Tensleep Sandstone and Madison Limestone. Both formations are known to contain gypsum or anhydrite, yet average water compositions are not saturated with respect to these two minerals. We increased calcium and sulphate concentrations for waters in both formations to values that lie within standard deviations and that yielded saturation with respect to gypsum and anhydrite. The results are plotted on Figure 4. By including these two values, several combinations of waters from two or three formations can be used to constrain the compositions of Big Spring and White Sulphur Spring. Clearly, the major element compositions that are available are insufficient to determine whether the thermal waters are a mixture of the Paleozoic aquifers. Similarly, the available major element geochemistry does not distinguish between the two models proposed for groundwater flow in the Thermopolis hydrothermal system (see discussion in section on Regional Hydrogeology and Groundwater Flow). Major, trace, and isotopic analyses of gasses as well as trace and isotopic analyses of waters have been successfully used to evaluate complex groundwater phenomena (Crossey et al., 2006; Crossey et al., 2009; Banerjee et al., 2011; Monjerezi et al., 2011;

Karlstrom et al., 2013; Williams et al., 2013) and may be prove valuable for understanding processes in the Thermopolis hydrothermal system.

The geochemistry of the Thermopolis hydrothermal system remained uniform over the year of this study. With one exception, no changes were observed in the chemistry or temperature of water samples collected through the four seasons, on consecutive months and days, or even during different times of the same day. The exception is a decrease in calcium and magnesium concentrations in Big Spring in December 2010, but we lack sufficient data to provide plausible explanations for this anomaly. This anomaly aside, our observations suggest that surface and shallow groundwater does not influence the geochemistry of the hydrothermal system.

In the previous section, we describe several anomalies in the historic data set for the aqueous geochemistry of Big Spring. These anomalies preclude a definitive interpretation of the geochemical evolution of Big Spring. Nonetheless, we speculate on potential interpretations that are consistent with the data set. Increases in sodium and chloride concentrations between 1906 and 1926 are consistent with mixing of waters from a siliciclastic formation and thermal waters at the source of Big Spring. The magnitude of the increase in both sodium and chloride are equivalent, a relationship consistent with both ions being controlled by the dissolution of halite. Increases in calcium and sulfate concentrations between 1926 and 1933 are consistent with mixing of waters from a formation containing gypsum or anhydrite and thermal waters at the source of Big Spring. The decrease in magnesium concentration in this same time frame is consistent with dilution by this same mixing event. The magnitude of the increase in both calcium and sulfate are roughly equivalent, a relationship consistent with both ions being controlled by the dissolution of gypsum or anhydrite. An historic geologic event of sufficient importance to affect crustal fluid-rock systems was the earthquake at Hebgen Lake, Montana. This event, however, took place in 1959, well after the geochemical anomalies observed in Big Spring. Events taking place between 1906 and 1926, and again between 1926 and 1933, of sufficient scale to affect the geochemistry of Big Spring have not been identified. Decreased concentrations measured in our study, relative to concentrations measured between 1933 and 1976, may reflect mixing of thermal waters

with more dilute waters. We lack sufficient data to develop a dilution model to test this hypothesis. In addition, an event taking place between 1976 and 2010 that may have caused this mixing has not been identified. Stable isotope and tritium analyses of spring waters and local formation waters may be helpful in testing this hypothesis.

CONCLUSIONS

This investigation, the first published geochemical analyses of the thermal waters of the Thermopolis hydrothermal system in more than 30 years, evaluates the aqueous geochemistry of this hydrothermal system in an historic and regional geochemical context. The following are conclusions from this investigation:

1) Thermal waters of three active hot springs, Big Spring, White Sulphur Spring, and Teepee Fountain, are similar in composition. The geochemistry of these thermal waters is characteristic of carbonate aquifers or rocks containing abundant carbonate minerals.

2) Previous studies postulate that the thermal waters for the Thermopolis hydrothermal system are a mixture of waters from Paleozoic formations. The major element analyses available for waters from these formations, however, are not of sufficient quality to determine whether the thermal waters are a mixture of the Paleozoic aquifers.

3) In the time frame of this study (one year), the water chemistry of Big Spring, White Sulphur Spring, and Teepee Fountain was constant through all four seasons, spanning spring snowmelt and recharge as well as late summer and fall dryness. This relationship is consistent with a deep source not influenced by shallow, local hydrogeology.

4) Several anomalies are evident in the historic data set for the aqueous geochemistry of Big Spring. Speculative interpretations of these anomalies include thermal waters at the source of Big Spring mixing with waters from a siliciclastic formation between 1906 and 1926 and mixing with waters from a formation containing gypsum or anhydrite between 1926 and 1933. Decreased concentrations measured in our study, relative to concentrations measured between 1933 and 1976, are consistent with mixing of thermal waters with more dilute waters. Sufficient data are not currently available to develop a dilution model to test this suggestion, and events taking place in these timeframes and of sufficient scale to affect the geochemistry of Big Spring have not been identified.

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Appendix 1. Methods.

Temperature, pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), and conductivity (C) for each spring were measured using a YSI Professional Plus handheld multiparameter meter. The instrument was calibrated before each trip into the field. Water samples were collected in 60-mL Nalgene® syringes that were pre-contaminated by triple rinsing with spring water from the respective spring, filtered through 0.45 μm Nalgene syringe filters using a 25mm surfactant-free cellulose acetate membrane, and stored in acid washed and triple rinsed 60-mL polyethylene bottles. One bottle was filled for cation analysis, and a second was filled for anion analysis. Cation samples were acidified with trace-metal grade nitric acid to pH 2. Sample bottles were subsequently sealed and stored in a refrigerated environment.

Major, minor, and trace cations were analyzed using inductively coupled plasma-optical emission spectrometer (ICP-OES) and inductively coupled plasma-mass spectrometer (ICP-MS). Anions were analyzed using ion chromatography. The alkalinity of the springs was measured in the field in April and June 2011 (Table 4) using a Hach® digital titrator (Model 16900) following U.S. Geological Survey procedures (Rounds, 2006). The alkalinity of the springs for the 2010 sampling events was calculated from the chemical analysis by charge difference; these results were comparable to the field measurements made in 2011. Charge balances were computed as the difference between the sum of cations and sum of anions normalized to the total, expressed as percent milliequivalents/kg. Saturation indices, the partial pressure of CO_2, and total dissolved inorganic carbon (Table 4) were calculated for each water sample using Geochemist's Workbench® v10.0, the b-dot ion activity model, and the resident database thermo.com.V8.R6+.dat (Bethke and Yeakel, 2014).