

Gas and Isotope Chemistry of Thermal Features in Yellowstone National Park, Wyoming



Scientific Investigations Report 2011–5012

FRONT COVER

USGS researchers sample gas from a fumarole of the Quagmire Group, Lower Geyser Basin.
(USGS photograph by Kahryn Flynn, September 21, 2005).

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By Deborah Bergfeld, Jacob B. Lowenstern, Andrew G. Hunt, W.C. Pat Shanks III, and William C. Evans

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Contents

Abstract.....	1
Introduction.....	1
Background and Previous Work	1
Early Work.....	1
Conceptual Models of the Yellowstone Geothermal System	3
Gas Isotope Signatures and Fluid Origins	3
Hydrocarbon Gases.....	4
Gas Chemistry.....	4
Objectives.....	4
Methods.....	5
Sampling.....	5
Analytical.....	6
Data Formats and Uncertainties: Table 2 Gas Analyses	7
Data Formats and Uncertainties: Table 3 Water Analyses	13
Results	13
Bulk Gas Chemistry.....	13
Gas to Steam Ratio (Xg).....	16
Isotopes	16
Discussion.....	18
Water and Steam Isotopes ($\delta^{18}\text{O}$ and δD)	18
Gas Chemistry.....	18
Summary.....	23
Acknowledgements.....	24
References.....	24
Appendix 1. Site photos and summary information for Yellowstone gas and water samples (attached file; http://pubs.usgs.gov/sir/2011/5012/sir2011-5012_appendixes/sir2011-5012_appendix1.pdf).	
Appendix 2. Google Earth KML file linked to sample locations (attached file; http://pubs.usgs.gov/sir/2011/5012/sir2011-5012_appendixes/sir2011-5012_appendix2.kmz/).	
Appendix 3. ArcGIS shape file with gas geochemical data and locations (attached file; http://pubs.usgs.gov/sir/2011/5012/sir2011-5012_appendixes/sir2011-5012_appendix3_gis.zip).	

Figures

1. Map showing sample locations (green dots) within this database and other locations mentioned in the text.....	2
2. Photos showing examples of sampled thermal features represented in this gas geochemistry database.....	5
3. Plot of δD vs. $\delta^{18}\text{O}$ relative to Vienna Standard Mean Ocean Water (VSMOW) for condensed steam from selected Yellowstone fumaroles and for hot and cold spring waters.	17
4. Histogram showing $\delta^{13}\text{C}$ values relative to the standard Vienna PeeDee Belemnite (VPDB) for CO_2 in Yellowstone gas.....	17

5. Histogram showing $^3\text{He}/^4\text{He}$ R_c/R_a values for 73 gas samples collected from Yellowstone	18
6. Pie charts demonstrate the differences among gas discharges at Yellowstone.....	19
7. Ternary diagram showing He, N_2 , and Ar relations for gas collected from fumaroles and frying pans	20
8. Ternary diagram showing He, CH_4 , and Ar relations for gas collected from fumaroles and frying pans	20
9. Map from Christiansen (2001) of the area around Norris Geyser Basin showing some of the gas-sample localities plotted as colored dots sized in proportion to the CH_4/He ratio	21
10. Plot showing mol percent CH_4 versus mol percent C_2H_6 for samples from Eastern Yellowstone, Washburn Hot Springs, Norris Geyser Basin, and Heart Lake.....	22
11. Plot showing the ethane to methane ratio (C_2/C_1) versus the $\delta^{13}\text{C}$ value of methane (C1) as normalized by the same ratio in the standard Vienna PeeDee Belemnite (VPDB), for gas collected from fumaroles, frying pans, and pools at Yellowstone	23

Tables

1. Details concerning sample groupings and water types as discussed in the text.....	6
2. Sample collection parameters and major and trace chemical data for gas samples collected within and around Yellowstone National Park, Wyoming during 2003 through 2009.....	8
3. Water chemistry, stable isotope values, and sample collection parameters for waters collected within and around Yellowstone Park, Wyoming, during 2003 through 2009.....	14
4. Statistical synthesis of individual gas species and radiogenic and stable isotope data for Yellowstone gas samples	16

Conversion Factors

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
 $^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:
 $^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$

Vertical coordinate information is referenced to the North American datum of 1983 (NAD 83).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

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By Deborah Bergfeld, Jacob B. Lowenstern, Andrew G. Hunt, W.C. Pat Shanks III, and William C. Evans

Abstract

This report presents 130 gas analyses and 31 related water analyses on samples collected from thermal features at Yellowstone between 2003 and 2009. An overview of previous studies of gas emissions at Yellowstone is also given. The analytical results from the present study include bulk chemistry of gases and waters and isotope values for water and steam ($\delta^{18}\text{O}$, δD), carbon dioxide ($\delta^{13}\text{C}$ only), methane ($\delta^{13}\text{C}$ only), helium, neon, and argon. We include appendixes containing photos of sample sites, geographic information system (GIS) files including shape and kml formats, and analytical results in spreadsheets. In addition, we provide a lengthy discussion of previous work on gas chemistry at Yellowstone and a general discussion of the implications of our results. We demonstrate that gases collected from different thermal areas often have distinct chemical signatures, and that differences across the thermal areas are not a simple function of surface temperatures or the type of feature. Instead, gas chemistry and isotopic composition are linked to subsurface lithologies and varying contributions from magmatic, crustal, and meteoric sources.

Introduction

Yellowstone National Park hosts an active hydrothermal system with more than 10,000 individual thermal springs, pools, and fumaroles (Fournier, 1989). These thermal features exist because of heat generated by intrusion and crystallization of magma beneath the Yellowstone Caldera and its surroundings coincident to an abundant water supply (Lowenstern and Hurwitz, 2008). The heat that is transferred upwards into voluminous groundwater reservoirs produces hydrothermal fluids that may boil on ascent, feeding surface hot springs and fumaroles. Gases in hot springs and fumaroles are sufficient in volume and flux that significant magmatic input is required, at least for the carbon dioxide (Werner and Brantley, 2003; Lowenstern and Hurwitz, 2008). The different gas species have a variety of potential sources in addition to magma (see, for example, Giggenbach and Poreda, 1993; Minissale and others, 1997; Lowenstern and Janik, 2003), including descending meteoric waters, as well as reactions with volcanic and nonvolcanic wallrocks and organic

material. The water and gas chemistry is also affected by high-temperature interaction with silicate rocks (Giggenbach, 1984; Hurwitz and others, 2010) and by biological activity at the surface, including respiration by thermophilic organisms that reside within and around the thermal features (see, for example, Nordstrom and others, 2006; Shock and others, 2010). The chemistry of gas emanations provides important clues about the history and ongoing process of magma degassing, metamorphism, water-rock interaction, hydrothermal reservoir conditions, and biological activity.

This report presents a database of gas and isotope chemistry for 130 samples collected from fumaroles, pools, and “frying pans” from areas within and around Yellowstone National Park. Some of the 130 analyses represent replicate samples collected back-to-back in different bottles on the same day, and others are samples collected from the same location in different years. All of the samples were collected in August or September from 2003 to 2009. This report focuses on gas-phase samples because they provide information on the underlying magmatic system and various crustal rocks. Dissolved gas concentrations, by contrast, are more likely to reflect solubility constraints at near-surface conditions, rather than conditions established deep in the system.

Following a discussion of previous work, we present a brief discussion of the general geochemistry of the collected gases. We also provide sufficient metadata (locations, photographs, and temperatures) to aid with interpretation of the chemical characteristics of the gases. Finally, we consider the systematic variations in gas concentrations and ratios and their significance for understanding the gas sources. Future publications will further develop interpretations and will discuss the implications for magmatism, crustal metamorphism, and hydrothermal processes.

Background and Previous Work

Early Work

Early trappers and explorers in the Yellowstone region recognized sulfurous odors and brimstone (sulfur-bearing) deposits, plus the “soda gas” (CO_2) emerging at Mammoth Hot Springs (fig. 1). Indeed, C.L. Heizmann, the chemist for

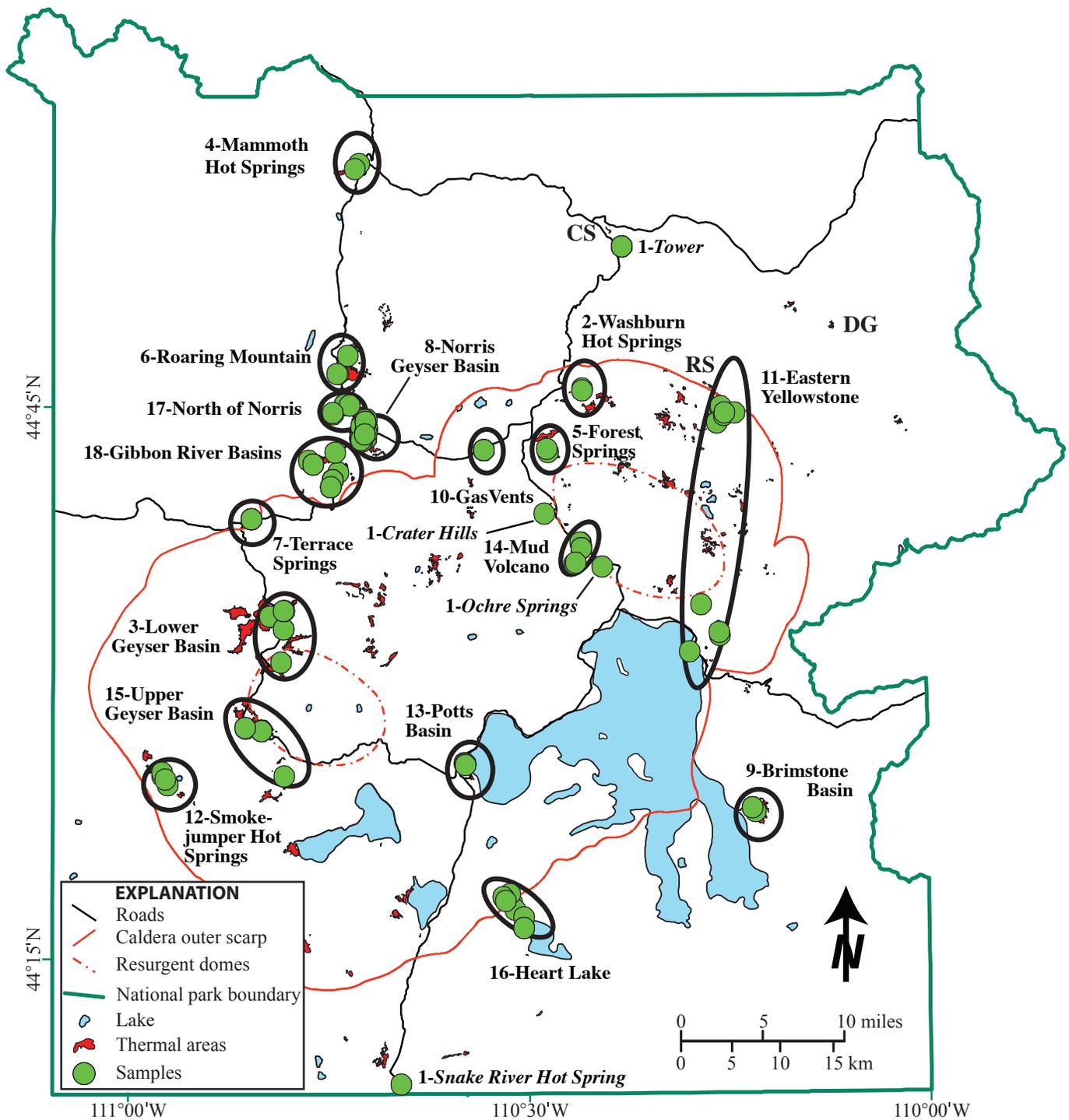


Figure 1. Map showing sample locations (green dots) within this database and other locations mentioned in the text. Sample groups 2–18 are circled by bold black lines and are labeled with the group name and group number as listed in table 1. Sample group 1 contains miscellaneous samples located in four areas that are shown in italicized text. CS=Calcite Spring, DG=Death Gulch, RS=Rainbow Springs.

the 1873 Jones Expedition was able to confirm the presence of both sulfur and carbonic gases (Jones, 1875). Gooch and Whitfield (1888) published a remarkable set of analyses of thermal waters, but they made no attempt to analyze gas bubbles emerging from the waters or nearby soils. Weed (1889) described gas vents along Cache Creek, dubbing the area “Death Gulch” (fig. 1) for the dead animals (including six deceased bears) that were found at the time to have succumbed to the effects of noxious gas. Jaggard (1899) later revisited and documented the gas vents of “Death Gulch,” and Traphagen (1904) analyzed the gases, finding lethal amounts of both CO₂ and H₂S within cracks and near ground level.

In his paper “Origin of the Thermal Waters in the Yellowstone National Park,” Hague (1911) reported gas analyses by F.C. Phillips of Pittsburgh, Pennsylvania. Most samples appear to have been contaminated by significant amounts of air, but many were dominated by CO₂ and some contained H₂S and CH₄. Hague (1911) argued that the thermal waters of Yellowstone were meteoric in origin and had descended a sufficient distance to acquire heat and solutes before ascending back to the surface. The waters were believed to be acidic at depth and subsequently neutralized through degassing of H₂S and CO₂.

It was not until the monumental work of Allen and Day (1935) that a detailed study of gases from Yellowstone National Park was completed. Their 525-page treatise presented detailed summaries of most of Yellowstone’s thermal areas, including water chemistry, flow rates, and heat discharge. Many of their measurements, especially with respect to spring and stream discharge, have not been redetermined in the subsequent 75 years. With respect to gas chemistry, Allen and Day (1935) provided analyses for most of the major species from 40 locations and showed that CO₂ dominated other gases, CO was essentially absent, and H₂S was the next most abundant gas after steam and CO₂. They recognized that little water flowed from the acid terrains, whereas considerable water flow could be found in the alkaline, Cl-rich thermal areas. They also noted more abundant gas associated with the acid waters; they were able to collect 1 liter of gas in about 6 minutes from acid waters, whereas it could take more than ten times that long to collect the same volume of gas from alkaline waters (Allen and Day, 1935, p. 90). Finally, Allen and Day (1935) noted that gases from alkaline waters were much richer in N₂ and other air-sourced gases. Their thinking was fundamentally different from that of Hague (1911), because they hypothesized that magmatic gas rose straight to the surface and was composed of superheated steam and CO₂ with minor amounts of H₂, CH₄, N₂, Ar, and H₂S. They thus believed that fumaroles, or steam vents, were features that discharged gases from depth. Alkaline waters issued in topographically low areas where groundwater was most abundant and could minimize the mass of rising acid gas. Higher areas with deeper groundwater were overwhelmed by fumarolic emanations, resulting in acid waters and acid-altered terrains. This model represented a great departure from that of Hague (1911), who envisioned that both acid and alkaline

waters were ultimately meteoric in origin, with alkaline waters as degassed or reacted equivalents of acid waters.

Conceptual Models of the Yellowstone Geothermal System

White (1957) provided a new conceptual view that differed from those of previous workers and could be applied to a variety of Yellowstone’s acid sulfate regions (his terminology) located close to areas bearing alkaline waters. He believed the acid sulfate waters (those acid waters high in sulfate but low in chloride) represented the steam boiled off alkaline waters. Condensation of the steam and shallow oxidation of H₂S (the latter also discussed by Allen and Day, 1935) created hot, acid-altered terrain. This theme was later expanded upon in White and others (1971), using abundant data from Yellowstone, including lessons learned from scientific drilling in Yellowstone during the late 1960s (White and others, 1975). Truesdell and Fournier (1976) and Fournier (1989) focused their efforts mainly on the neutral chloride fluids, finding evidence that most of the waters in and near the Yellowstone Caldera could be derived from a single parent fluid at 340°C and with ~400 mg/l Cl. Waters boiled off this fluid would rise in acid sulfate regions. Divergent mixing, cooling, and boiling paths would result in the diversity of neutral to alkaline waters in the geyser basins.

Morgan and others (2003) and Morgan and Shanks (2005) suggested that lava flows exert a fundamental control on the locations of thermal basins through lateral flow of deep-seated waters in basal breccias, resulting in venting at edges of lava flows in drainage basins. Hurwitz and others (2007, 2010) noted the pronounced differences in river chemistries around the caldera, attributing the variability to significant (shallow) lateral migration of originally deep Cl-rich geothermal fluids that emerge at the surface primarily at low elevations along the Firehole, Gibbon, and Snake rivers, near Heart Lake, and at West Thumb. The acid-sulfate terrains, mostly concentrated in the eastern part of the caldera, reflect areas of deep boiling and gas discharge (Fournier, 1989). Nordstrom and others (2006, 2009) discussed the detailed geochemistry of H₂S oxidation in acid sulfate systems, the formation of abiogenic sulfur mounds, and oxidation and reduction reactions, some biotic, that form sulfuric acid, thiosulfate, polythionate, and sulfate. Nordstrom and others (2009) classified acid sulfate waters as “MG,” reflecting their inferred origin as meteoric (M) waters fluxed with hot gas (G).

Gas Isotope Signatures and Fluid Origins

With the development of tools in nuclear isotope geochemistry following World War II, many researchers began to apply isotopic analyses to understanding the origins of the geothermal waters and gases of Yellowstone. Craig (1953) looked at the isotopes of carbon from numerous gases, carbonates, organic materials, and other sources in an overview of the systematics of carbon at Yellowstone. The δ¹³C value of

CO₂ in Yellowstone gases averaged –2.8 per mil, which was similar to values from limestone but greater than that seen in igneous rocks (at that time thought to be < –20 per mil), causing him to conclude that the gases were likely sourced primarily from limestone. Later work on hydrogen and oxygen isotopes (Craig and others, 1956) showed that water and steam from Yellowstone were almost entirely of meteoric origin. Gas ratios determined by Mazor and Wasserburg (1965) and later by Gunter and Musgrave (1966) also pointed to a clear meteoric origin of the waters, because noble gas ratios displayed atmospheric values. Excess He was attributed to radioactive decay of crustal materials. Later studies on gases from geothermal drillholes in Yellowstone confirmed the presence of radiogenic He and Ar, but no evidence was found for crustal or magmatic sources of H₂O (Mazor and Fournier, 1973).

Craig and others (1978) were the first to document high ³He/⁴He ratios in Yellowstone gases, finding R/R_a values (the ³He/⁴He ratio of the sample relative to that of air) as high as 15 and attributing this to the hotspot setting. They also remarked that in some areas (for example, Mud Volcano) there was minimal influence of continental crust on the mantle-derived He isotope signatures. Further evidence for a diversity of gas sources came from subsequent studies of noble gases. Kennedy and others (1985, 1987) undertook a detailed study of the noble gas isotope systematics, and they found evidence for three primary end members—atmospheric, crustal and magmatic, the latter best exemplified by gases from Mud Volcano. The crustal endmember had ⁴⁰Ar/⁴He of 0.245 (the * denoting radiogenic origin), consistent with a K/U source ratio of about 14,000 (Kennedy and others, 1985). Results from Werner and others (2008) extended the K/U ratio to a value as low as 2,000 for gas from the Hot Spring Basin region, consistent with derivation from limestone or quartz-rich sedimentary rocks.

More local studies undertaken on the Lower Geyser Basin (Kennedy and others, 1987) and in Shoshone Geyser Basin (Hearn and others, 1990) found that R/R_a values were correlated with bicarbonate concentrations in spring waters. Both groups concluded that degassing of the waters lowered their He (and bicarbonate) concentrations, allowing greater influence of mixing with crustal (radiogenic) He (see also Fournier and others, 1994). The most magmatic He-isotope signatures were retained by samples that cooled without considerable boiling during upflow. Evans and others (2006) undertook a detailed study of the chemistry of waters and gases from springs northeast of the Yellowstone Caldera, searching for evidence of an inferred CO₂-rich gas body thought to be located between Norris Junction and Hebgen Lake (Husen and others, 2004). The low flux of dead (old) carbon and low R/R_a provided little evidence for the accumulation of magmatic or metamorphic gas in that region.

Hydrocarbon Gases

Other workers have focused on the origin of organic gases such as methane (CH₄) and higher hydrocarbons. Such gases at Yellowstone are especially abundant in eastern areas of the

park, including those known to produce small seeps of liquid petroleum (Love and Good, 1970). Des Marais and others (1981) demonstrated convincingly that the decomposition of sediments containing organic material was responsible for generating methane. They noted that the ratio of methane to higher hydrocarbons was far lower than would be predicted by full equilibration of C-O-H gases under geothermal conditions and were consistent with disequilibrium breakdown of organic matter in wallrocks. Clifton and others (1990) studied “hydrothermal” petroleum and inferred Eocene mudstone sources for Rainbow Springs (fig. 1), whereas petroleum found at Calcite Spring was inferred to be derived from the Permian Phosphoria Formation and recent sediments filling the valley of the Yellowstone River. Lorenson and others (1991) published hydrocarbon gas and isotopic analyses from these and a variety of other springs and seeps throughout the park.

Gas Chemistry

After Allen and Day (1935), few subsequent studies have reported complete analyses of gas compositions. Hearn and others (1990) published nine full analyses of gases from hot springs and fumaroles sampled at Shoshone Geyser Basin in 1982 and 1986. Sheppard and others (1992), using results from sites sampled between 1974 and 1986, demonstrated that gases obtained from large pools were unlikely to yield reliable results because of differential gas solubility in the near-surface water. They concluded that most Yellowstone gases represent a mixture of gas derived from air-saturated meteoric water with gas containing a He-rich crustal endmember, consistent with the findings of Kennedy and others (1985). Werner (2002) and Werner and Brantley (2003) provided 15 full analyses of gases from Yellowstone in conjunction with calderawide estimates of CO₂ flux. Goff and Janik (2002) compared nine of these samples and three others from Yellowstone with those from the Valles and Long Valley calderas and concluded that at Yellowstone, gas was derived from air-saturated meteoric water and a He-rich endmember that could originate from either mantle or crustal materials. Relative CH₄ abundances were higher than in gases from the Valles and Long Valley calderas. Werner and others (2008) demonstrated that Hot Spring Basin gases were relatively rich in rock-derived crustal components such as He, CH₄, and H₂.

Objectives

Three different types of features—fumaroles, “frying pans,” and thermal pools (fig. 2)—were sampled to provide a comprehensive overview of gas geochemistry in Yellowstone National Park and to provide information on the gas geochemistry of the hydrothermal and magmatic systems. We sought fumarole samples (steam and gas vented through cracks or holes in the ground) whenever possible, because they provide the best samples of deep-seated gases. Fumaroles only exist where the temperature of the thermal feature equals

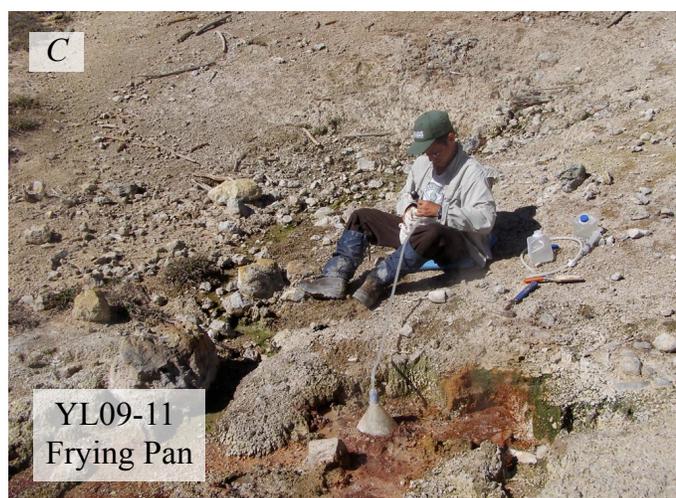
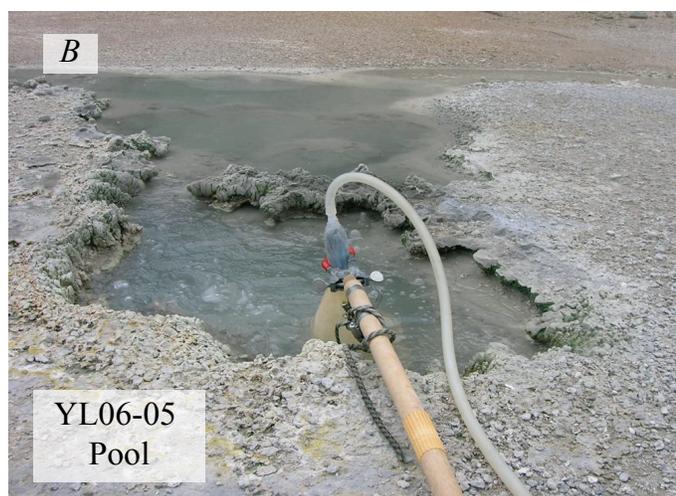


Figure 2. Photos showing examples of sampled thermal features represented in this gas geochemistry database. *A*, Fumaroles are features where steam/gas emerges from dry ground or through a crack. *B*, Pools and springs are features where water issues from the ground (with associated gas bubbles) or where gas rises through standing water. *C*, “Frying pans” are areas of sizzling ground with abundant steam/gas discharge and small amounts of liquid water.

or exceeds that of the local boiling point of water. In thermal areas where the subsurface is water saturated, one often finds a terrain of “frying pans” (sizzling ground), features whose temperatures are close to the boiling point. In locations where there were no fumaroles (or locations where an existing fumarole could not be sampled) frying pans provided the next-best sampling point. Some areas lack fumaroles and frying pans and instead have pools, where gas bubbles emerge from the surface of liquid water. Though some pools are connected to flowing springs, other pools lack outlet channels and consist of stagnant or convecting water. Gases rising through such pools and through frying pans cannot be attributed simply to boiling of the water in the pools but must come from depth.

Locations for gas samples are shown in figure 1, a map of Yellowstone National Park with dots for individual samples and showing sample groups as defined in table 1 and keyed to the remainder of the tables and figures in the manuscript. For the purpose of this report, water types of specific thermal areas are defined as follows: (1) acid sulfate waters are waters with $\text{pH} < 5$ and sulfate as the primary anion, (2) neutral Cl waters have $\text{pH} > 5$ and Cl as the primary anion, and (3) Na and Ca carbonate waters have carbonate as the dominant anion, with either Na or Ca as the primary cation. Thermal areas with more than one water type are denoted as “various” in table 1. Other papers (for example, Fournier, 1989; Nordstrom and others, 2009) provide more detailed descriptions of water chemistry. Photographs and summary tables for each gas sample are provided in appendix 1. Appendixes 2 and 3 contain KML and shape files to be used with Google Earth and ArcGIS software programs, respectively.

Methods

Sampling

Gas, water, and steam-condensate samples were collected and analyzed using standard field and laboratory methods. Sampling sites at locations with multiple features were selected on the basis of comparison of vent temperatures and the strength of gas outflow. At all locations, temperatures were measured using a K-type thermocouple and digital thermometer. At warm and cold springs, pH was measured using a calibrated meter, and indicator strips were used at hot springs and pools.

Bulk gas composition was determined following methods outlined in Fahlquist and Janik (1992). Fumarole samples were collected via a titanium tube, whereas a funnel fitted with flexible tubing was used to collect gas from frying pans and pools (fig. 2). Silicone tubing was used to connect the funnel or titanium tube to the sample bottle for all samples before the 2005 field season. Tygon tubing was used for some samples in 2005, and in all subsequent years. At fumaroles, a separate aliquot of condensed steam was often collected into glass bottles for stable-isotope analysis. The steam was condensed by adding a length of Tygon tubing to the sampling

Table 1. Details concerning sample groupings and water types as discussed in the text.

Group	Group Name	No. Samples	Water Type
1	Miscellaneous	6	Various
2	Washburn Hot Springs	2	Acid Sulfate
3	Lower Geyser Basin	6	Neutral Cl
4	Mammoth Hot Springs	2	Ca Carbonate
5	Forest Springs	2	Acid Sulfate
6	Roaring Mtn/Amphitheater Springs	3	Acid Sulfate
7	Terrace Springs	3	Na Carbonate
8	Norris Geyser Basin	32	Various
9	Brimstone Basin	3	Acid Sulfate
10	Gas Vents, Norris-Canyon Road	4	Acid Sulfate
11	Eastern Yellowstone	12	Acid Sulfate
12	Smokejumper Hot Springs	4	Acid Sulfate
13	Potts Basin	3	Neutral Cl
14	Mud Volcano	8	Acid Sulfate
15	Upper Geyser Basin	9	Neutral Cl
16	Heart Lake	8	Neutral Cl
17	North of Norris Geyser Basin	7	Various
18	Gibbon River Basins	10	Various

apparatus and placing it in a bucket or beaker of cold water until a sufficient amount of steam emerging from the fumarole had condensed within the line. For gas-rich samples we used a small hand pump to facilitate a continuing flow of steam into the line. The condensed steam was gravity-fed into the sample bottle.

Gases collected for analysis of noble gas concentrations and isotopic ratios were collected from the titanium tube or funnel into copper tubing that was then sealed at both ends using refrigerator clamps. For these types of samples Tygon tubing was used for all connections in all years.

Water samples for bulk chemistry were collected through a 0.45- μm filter into plastic bottles that were first prerinsed with filtered water. Samples for cation analyses were preserved with high-purity nitric acid by dropwise addition until a pH < 2 was obtained. Other nonfiltered water samples were collected in glass bottles for alkalinity titrations and stable isotope analyses of δD and $\delta^{18}\text{O}$.

Analytical

Gas samples were analyzed for their bulk composition at the USGS Volcano Gas Geochemistry Laboratory in Menlo Park, California. The head-space gases H_2 , He, Ar, O_2 , N_2 , CH_4 , and other hydrocarbons were analyzed using a Varian gas chromatograph with a dual-injection system using Ar and He carrier gases. Concentrations of the absorbed soluble gases were determined by wet-chemical techniques, including ion chromatography (Dionex ICS-2000) for HCl, HF, and H_2S (after conversion to sulfate), ion selective electrode (NH_3),

and direct measurement of CO_2 on a vacuum extraction line, following acidification of the NaOH solution. Replicate analysis of NaOH blanks (that is, from prepared bottles with no sample added) provided background concentrations of CO_2 , Cl⁻, F⁻, and SO_4^{2-} that were used to correct measured values. The background concentrations of Cl⁻ and SO_4^{2-} were larger in 2003–5 than in subsequent years when we began using commercially prepared ion exchange columns. Until 2006, CO_2 concentrations were quantified by pipetting an aliquot of the NaOH solution and 0.5 ml of H_2O_2 into an extraction vessel and evolving the CO_2 using phosphoric acid, following the standard procedure of McCrea (1950). The amount of CO_2 was quantified by a mercury manometer, and the sample was then transferred to a bottle for isotopic analysis. In 2006 we changed the procedure so that immediately after the sample bottle was opened an aliquot of NaOH was drawn into a syringe and then injected through a septum into an evacuated bottle. The syringe was weighed before and after injection, providing an accurate measure of the NaOH content. An additional 0.5 ml of H_2O_2 was similarly injected, and the sample was allowed to sit overnight. The following day a sufficient amount of 5 N H_2SO_4 was added to liberate the CO_2 . The gas was purified and quantified using a digital pressure gauge on an extraction line using standard cryogenic techniques, and the CO_2 was then transferred to a bottle for stable isotope analysis. This procedure reduced the exposure time of the NaOH sample solution to the atmosphere and improved quantification of the amount of NaOH over the pipette method.

On average the blank NaOH solutions contained 6 μmol of CO_2 per ml NaOH. The CO_2 content of the blanks most

likely reflects exposure of the solution to atmospheric CO₂ during bottle preparation. Results of five analyses of the blank-generated CO₂ had $\delta^{13}\text{C-CO}_2$ values between -21.1 and -17.6 per mil, the low $\delta^{13}\text{C}$ values resulting from kinetically controlled isotopic fractionation when atmospheric CO₂ ($\delta^{13}\text{C} \approx -8$ per mil) diffuses into the NaOH (Fritz and others, 1985). For most samples the influence of this small amount of atmospherically derived CO₂ on the final carbon isotope composition is not detectable. Comparison of $\delta^{13}\text{C-CO}_2$ values from replicates where one sample is collected in NaOH and a second sample is collected in an evacuated bottle show that, at CO₂ concentrations greater than 50 μmol per ml NaOH, there is no discernable isotopic shift. All samples with CO₂ isotope data in table 2 have concentrations above this cutoff value.

Starting in 2008, an aliquot of the head-space gas from samples with sufficient CH₄ was reserved for carbon isotopic analysis. Water and CO₂ were removed from the bulk gas using standard cryogenic techniques. The remaining gas, mostly N₂ and CH₄, was introduced to a section of the vacuum line containing a copper-oxide furnace and the temperature raised to 800°C (Kiyosu and Krouse, 1989). To ensure total conversion of CH₄ to CO₂ the gas was held at 800°C for 2 hours. Upon completion, the temperature was lowered and the furnace cooled slowly to 400°C. After cooling, the volume of produced CO₂ was determined and the sample was sent to the USGS lab in Reston, Virginia, for $\delta^{13}\text{C}$ analysis.

Isotope analyses were performed at several laboratories. Carbon isotope analyses were performed at USGS laboratories in Menlo Park and Reston. The ³He/⁴He determination was run at the USGS Noble Gas Laboratory in Denver, Colorado, as discussed in Werner and others (2008). δD and $\delta^{18}\text{O}$ analyses of waters (δD_w , $\delta^{18}\text{O}_w$) and condensed steam (δD_s , $\delta^{18}\text{O}_s$) were performed at the USGS laboratory in Denver. During 2003-8 the water and steam isotope analyses were performed using techniques outlined in Coleman and others (1982) and Epstein and Mayeda (1953). In 2009 these analyses were performed by laser cavity ring-down spectroscopy.

Anion concentrations were determined using ion chromatography (Cl⁻, F⁻, SO₄²⁻) and titration (HCO₃⁻). Cation concentrations were determined using either inductively coupled plasma mass spectroscopy (Perkin Elmer ELAN 6000, 2003-7) or inductively coupled plasma optical emission spectroscopy (Thermo Scientific icap 6000, 2008-9) at USGS laboratories in Menlo Park.

Data Formats and Uncertainties: Table 2 Gas Analyses

Below we outline the data columns in table 2 and information relevant for interpretation of values and their related uncertainties.

Sample: Alpha-numeric codes begin with YL followed by a two-digit year code (03 for 2003, for

example), a hyphen, and a sample number for that year.

Location: Informal name for the sampled feature. The name could be a defined thermal feature or could indicate simply that the sample was taken in the same general location. When we sampled an actual thermal feature denoted in the Yellowstone Thermal Features database (<http://www.rcn.montana.edu/resources/features/features.aspx?nav=11>), we list the name of that feature in the “YNP Thermal Features Database” column.

Group: One of 18 groups defined for the purpose of explication and plot generation. Except for group 1 (Miscellaneous) and group 11 (Eastern Yellowstone), samples in a group are generally closely located. The groups shown below are also described and categorized in table 1.

1. Miscellaneous
2. Washburn Hot Springs
3. Lower Geyser Basin
4. Mammoth Hot Springs
5. Forest Springs
6. Roaring Mountain/Amphitheater Springs
7. Terrace Springs
8. Norris Geyser Basin
9. Brimstone Basin
10. Gas Vents (Norris-Canyon Road)
11. Eastern Yellowstone
12. Smokejumper Hot Springs
13. Potts Basin
14. Mud Volcano
15. Upper Geyser Basin
16. Heart Lake
17. North of Norris Geyser Basin
18. Gibbon River Basins

Date Sampled: In month/day/year format (mm/dd/yyyy).

Feature: Split into three types: (1) fum (fumarole), (2) fry (frying pan), and (3) pool (pools and springs). Some fumaroles may be steaming ground or subboiling gas seeps.

Temp: Temperature in degrees Celsius. Temperature can be reproducibly measured to within 0.1°C, but accuracy may be limited to ~0.5°C because of temperature variability within the feature and instrumental variations.

Easting: East-west location in Universal Transverse Mercator (UTM) coordinate system, Zone 12. Datum is NAD83 (nearly identical to WGS84). Units are in meters. Uncertainties are generally ~3 m.

Northing: North-south location in Universal Transverse Mercator (UTM) coordinates, Zone 12. Datum is NAD83 (nearly identical to WGS84). Units are in meters. Uncertainties are generally ~3 m.

Xg%: Mole percent gas relative to gas plus steam. A sample with no steam would have a value of 100 (for example,

Table 2. Sample collection parameters and major and trace chemical data for gas samples collected within and around Yellowstone National Park, Wyoming during 2003 through 2009.

[bdl, below detection limit; a blank cell indicates that an analysis was not attempted]

Sample number	Location	Group	Date	Feature	Temp °C	Easting meters	Northing meters	Xg (%)	CO ₂ mol%	H ₂ S mol%	NH ₃ mol%	He mol%	H ₂ mol%	Ar mol%	O ₂ mol%	N ₂ mol%	CH ₄ mol%	C ₂ H ₆ mol%	HCl mol%	R/Ra	Rc/Ra
YL03-01A	Lone_Star	15	09/04/2003	fry	94.0	515429	4918413	0.11	87.6	3.68	0.081	0.0041	0.770	0.1583	0.49	6.3	0.88	0.00183	bdl	7.32	7.37
YL03-02A	Fountain_Paint_Pot	3	09/05/2003	fum	111.1	515386	4933083	0.48	94.3	0.45	0.020	0.0051	0.008	0.1014	0.28	4.0	0.85	0.00103	bdl	6.11	6.13
YL03-03A	Black_Sands1	15	09/05/2003	fry	92.2	511542	4923256	0.50	95.3	0.25	0.028	0.0019	0.023	0.0959	0.48	3.4	0.42	0.001	bdl		
YL03-04A	Black_Sands2	15	09/05/2003	pool	76.1	511628	4923190	82.	77.6	0.22	0.002	0.0093	bdl	0.4473	2.70	17.4	1.7	0.00226	bdl		
YL03-05B	Near_DB	8	09/06/2003	fum	94.7	523214	4952111	0.05	75.1	7.6	0.037	0.0021	0.598	0.3480	1.60	14.5	0.14	0.00041	bdl	6.85	7.17
YL03-06B	Green_Dragon	8	09/06/2003	pool	88.6	523196	4951898	38.	84.5	0.40	0.002	0.0045	0.091	0.3430	0.60	13.8	0.30	0.00115	bdl		
YL03-07	Son_of_Green_Dragon	8	09/06/2003	fum	94.1	523208	4952035	0.15	90.2	3.94	0.007	0.0012	0.318	0.1210	0.48	4.8	0.086	0.00011	bdl	6.87	7.04
YL03-08	Dishwater	8	09/06/2003	pool	89.4	523384	4952086	9.4	91.0	0.60	0.005	0.0024	0.376	0.1733	0.59	6.8	1.7	0.00058	0.26		
YL03-09B	Beryl_Spring	18	09/07/2003	fum	99.6	520077	4947298	1.1	98.3	0.83	0.009	0.0011	0.141	0.0176	0.0005	0.73	0.018	0.00001	bdl	12.34	12.40
YL03-10B	Black_Growler	8	09/07/2003	fum	93.6	523502	4952728	0.30	93.6	2.91	0.139	0.0016	0.388	0.0716	0.009	2.8	0.10	0.00041	bdl	7.29	7.35
YL03-11B	Black_Pit	8	09/07/2003	pool	82.3	523588	4952139	80.	94.0	0.69	0.0006	0.0023	0.649	0.0954	0.52	3.9	0.16	0.00063	bdl		
YL03-12A	Porcelain_Terrace1	8	09/07/2003	fum	93.9	523746	4953112	1.0	96.9	2.00	0.0012	0.0045	0.333	0.0134	0.0008	0.47	0.28	0.00063	bdl		
YL03-13A	Nymph_Lake_new_feature	17	09/08/2003	fum	93.6	521471	4955495	0.93	97.7	0.92	0.021	0.0041	0.232	0.0257	0.013	1.02	0.064	0.00014	bdl	4.93	4.94
YL03-14B	Terrace_Springs	7	09/08/2003	pool	63.3	512184	4944102	87.	99.8	bdl	bdl	0.0003	0.001	0.0054	0.036	0.17	0.0003	bdl	bdl	7.92	7.93
YL03-15A	W_Nymph_Lake_Thermal_Area1	17	09/09/2003	pool	82.0	520335	4954609	44.	97.7	0.40	bdl	0.0080	0.187	0.0389	0.028	1.5	0.14	0.00018	bdl	6.32	6.32
YL03-16A	W_Nymph_Lake_Thermal_Area2	17	09/09/2003	fry	92.0	520244	4954683	2.8	98.5	0.73	0.001	0.0039	0.161	0.0125	0.0002	0.52	0.071	0.00009	bdl	6.26	6.26
YL03-17A	Conoco	15	09/10/2003	fum	94.5	513205	4922954	0.20	91.3	1.55	0.039	0.0021	0.074	0.1468	0.81	5.6	0.48	0.0008	bdl	7.72	7.82
YL03-18A	Smokejumper1	12	09/12/2003	pool	85.0	503793	4917530	75.	83.0	1.06	0.001	0.0146	5.268	0.2254	0.30	8.7	1.4	0.00323	0.01		
YL03-19A	Smokejumper2	12	09/12/2003	fum	92.1	503260	4918509	0.47	89.5	3.86	0.020	0.0069	2.275	0.0924	0.003	3.5	0.69	0.00175	bdl	5.49	5.50
YL03-20	Smokejumper3	12	09/12/2003	fum	92.1	503273	4918792	0.36	89.0	4.09	0.008	0.0058	2.627	0.0846	0.013	3.6	0.57	0.00143	bdl		
YL03-21A	Smokejumper4	12	09/12/2003	fry	92.1	503559	4918096	0.29	88.3	4.44	0.026	0.0072	3.127	0.0841	0.032	3.3	0.69	0.00175	bdl	5.62	5.64
YL04-01	Black_Pit	8	09/13/2004	fum	92.6	523588	4952139	0.68	97.6	0.59	0.058	0.0022	0.484	0.0268	0.002	1.1	0.14	0.00073	0.002		
YL04-02	nr_Gibbon_R1	8	09/13/2004	pool	84.0	523658	4954007	4.7	96.5	1.44	0.008	0.0037	0.546	0.0240	0.0005	0.94	0.29	0.00884	0.201		
YL04-03	nr_Gibbon_R2	8	09/13/2004	pool	72.8	523680	4954101	93.	97.5	1.29	bdl	0.0031	0.324	0.0121	0.003	0.50	0.34	0.02172	0.005		
YL04-04	Nymph_Lake_new_feature	17	09/13/2004	fry	93.0	521444	4955530	1.2	97.8	0.67	0.007	0.0045	0.195	0.0278	0.0009	1.2	0.073	0.00014	0.02	4.74	4.75
YL04-05	Conoco	15	09/14/2004	fum	94.3	513182	4922973	0.20	93.3	1.05	0.011	0.0022	0.088	0.1245	0.10	4.8	0.50	0.00055	0.013	7.39	7.45
YL04-06	Bison_Kill	8	09/14/2004	pool	8.5	523471	4954042	61.	96.1	0.04	bdl	0.0013	0.0003	0.0683	0.68	3.0	0.14	0.00446	0.002	3.26	3.28
YL04-07	Bison_Flat1	8	09/14/2004	fum	92.9	523527	4953778	2.9	97.1	1.87	bdl	0.0046	0.023	0.0158	0.001	0.66	0.29	0.00564	0.003		
YL04-08	Back_Basin1	8	09/15/2004	fum	nm	523182	4952090	0.21	94.3	2.17	0.008	0.0020	0.268	0.0739	0.006	3.0	0.12	0.00026	0.018		
YL04-09	Back_Basin2	8	09/15/2004	pool	67.4	522963	4952193	92.	93.8	0.39	bdl	0.0015	0.011	0.1537	0.024	5.5	0.10	0.0002	0.004	7.66	7.81
YL04-10	Green_Dragon	8	09/15/2004	pool	76.8	523197	4951894	3.1	93.9	0.92	0.001	0.0026	0.430	0.0661	0.057	4.4	0.17	0.00075	0.002		
YL04-11	Steamboat_mud_volcano	8	09/15/2004	fum	92.8	523502	4952272	0.56	96.7	2.31	0.082	0.0021	0.386	0.0098	0.004	0.38	0.14	0.00208	bdl		
YL04-12	Porcelain_Terrace2	8	09/15/2004	fum	92.6	523732	4953033	1.0	97.1	1.29	0.001	0.0041	0.498	0.0206	0.0006	0.80	0.26	0.00144	0.006	4.48	4.48
YL04-13	Hundred_Springs_Plain	8	09/15/2004	pool	89.1	523113	4953330	23.	93.9	0.23	0.0003	0.0057	0.556	0.1180	0.047	4.8	0.33	0.00172	0.036	6.20	6.22
YL04-14	Beryl_Spring	18	09/16/2004	fum	93.1	520093	4947311	0.76	95.6	0.70	0.015	0.0007	0.083	0.0604	0.017	3.5	0.0100	0.00001	0.014	11.57	12.13
YL04-15	Devils_Den	1	09/16/2004	fum	27.2	549077	4971336	89.	98.0	1.08	0.0002	0.0006	0.002	0.0071	0.003	0.30	0.59	0.01778	0.01	0.84	
YL04-17	Sylvan_Springs1	18	09/17/2004	pool	22.4	517878	4949941	87.	98.6	0.16	bdl	0.0034	0.134	0.0253	0.005	1.1	0.023	0.00002	0.001	7.25	7.32
YL04-19	Sylvan_Springs2	18	09/17/2004	fum	97.8	518326	4949582	6.5	99.0	0.47	0.0004	0.0035	0.142	0.0075	0.0005	0.32	0.022	0.00002	bdl	7.13	7.14
YL04-20	Sylvan_Springs3	18	09/17/2004	fry	91.9	518326	4949582	3.9	98.9	0.45	bdl	0.0033	0.117	0.0114	0.0005	0.48	0.021	0.00002	0.003		
YL04-21	Gas_Vents_Norris_Canyon_Rd	10	09/18/2004	fum	92.1	535329	4951004	1.5	97.3	1.33	0.0003	0.0048	0.031	0.0258	0.002	1.02	0.32	0.00154	0.012	5.07	5.08
YL04-22	Artist_Paintpot	18	09/18/2004	fry	91.7	520838	4948760	0.16	87.9	0.66	0.005	0.0013	0.079	0.1971	2.70	8.4	0.039	0.00065	0.026	10.02	10.40
YL05-01	Black_Pit	8	09/13/2005	fum	91.7	523589	4952144	0.92	97.7	0.73	0.025	0.0032	0.624	0.0124	0.0007	0.45	0.21	0.00159	0.222	6.48	6.48
YL05-02	Terrace_Springs	7	09/13/2005	pool	62.3	512184	4944102	55.	99.7	0.01	bdl	0.0004	0.0001	0.0086	0.058	0.25	0.0003	0.00015	0.005		
YL05-03	Frying_Pan_Spring	17	09/14/2005	fry	91.8	521979	4955476	1.5	98.7	0.49	0.006	0.0042	0.368	0.0101	0.0006	0.38	0.087	0.00051	bdl		
YL05-04	Gibbon_River_Bridge	18	09/14/2005	fum	93.4	520295	4947980	3.0	99.3	0.34	bdl	0.0016	0.195	0.0039	0.0005	0.17	0.029	0.00038	0.006	12.14	12.15
YL05-05	Conoco	15	09/14/2005	fum	92.5	513181	4922972	0.18	96.0	0.72	bdl	0.0026	0.119	0.0744	0.005	2.5	0.61	0.00266	0.007		
YL05-06	Back_Basin3	8	09/15/2005	fum	92.6	523170	4952046	0.09	93.4	2.74	bdl	0.0020	0.345	0.1088	0.011	3.2	0.12	0.01314	bdl	7.26	7.31
YL05-07	Back_Basin4	8	09/15/2005	pool	87.4	523011	4952117	82.	91.1	0.72	bdl	0.0021	0.001	0.2227	0.002	7.8	0.10	0.00181	0.002		
YL05-08	Black_Growler	8	09/15/2005	fum	93.6	523496	4952728	0.53	97.7	1.11	0.011	0.0029	0.529	0.0141	0.001	0.49	0.17	0.00146	bdl		
YL05-09	Bison_Flat2	8	09/16/2005	fum	93.9	523538	4953830	1.7	97.6	1.53	bdl	0.0052	0.122	0.0113	0.0006	0.41	0.32	0.00726	bdl		
YL05-10	Nymph_Lake_new_feature	17	09/16/2005	fum	93.5	521456	4955507	2.7	98.9	0.45	0.0008	0.0044	0.224	0.0081	0.0004	0.30	0.073	0.00034	bdl	4.71	4.71
YL05-11	Chocolate_Pots	18	09/16/2005	pool	52.5	520496	4950780	93.	98.5	0.002	bdl	0.0013	0.0001	0.0401	0.014	1.4	0.033	0.00044	bdl		
YL05-12	Sulphur_Caldron1	14	09/17/2005	pool	68.9	544992	4941758	94.	99.3	0.16	bdl	0.0021	0.139	0.0077	0.016	0.36	0.031	bdl	0.001	14.97	14.98
YL05-13	Mud_Geyser	14	09/17/2005	fum	112.9	545055	4941205	11.	99.5	0.14	0.0008	0.0022	0.078	0.0035	0.0002	0.21	0.042	0.00011	0.006	15.29	15.29
YL05-13A	Mud_Geyser	14	09/17/2005	fum	112.9	545056	4941209	14.	99.5	0.15	0.0003	0.0022	0.075	0.0032	0.0001	0.20	0.041	0.00010	bdl		
YL05-14	Roaring_Mountain1	6	09/19/2005	fum	92.7	520861	4958599	2.9	98.9												

Table 2. Sample collection parameters and major and trace chemical data for gas samples collected within and around Yellowstone National Park, Wyoming during 2003 through 2009.—Continued

Sample number	Location	Group	Date	Feature	Temp °C	Easting meters	Northing meters	Xg (%)	CO ₂ mol%	H ₂ S mol%	NH ₃ mol%	He mol%	H ₂ mol%	Ar mol%	O ₂ mol%	N ₂ mol%	CH ₄ mol%	C ₂ H ₆ mol%	HCl	R/Ra	Rc/Ra
YL06-03		HSB3	11 08/29/2006	fry	91.4	558752	4954838	2.4	90.0	2.08	0.006	0.0083	6.969	0.0050	0.010	0.16	0.76	0.01546	bdl		
YL06-04		HSB4	11 08/29/2006	fum	93.4	558890	4955349	3.7	90.7	1.82	0.146	0.0079	5.764	0.0041	0.004	0.10	1.4	0.04646	0.001	5.10	5.10
YL06-05		HSB5	11 08/29/2006	pool	76.9	558925	4955398	88	91.1	1.76	bdl	0.0090	3.984	0.0365	0.010	1.5	1.5	0.04767	0.005		
YL06-06		HSB6	11 08/30/2006	fry	90.1	559263	4954529	0.74	91.2	3.09	0.749	0.0045	4.362	0.0061	bdl	0.20	0.36	0.01008	bdl	5.67	5.69
YL06-07		HSB7	11 08/30/2006	fum	90.9	560345	4954787	0.70	92.1	4.31	0.006	0.0029	0.049	0.0296	0.004	2.3	1.10	0.02742	0.014	4.63	4.71
YL06-08		HSB8	11 08/30/2006	pool	68.1	559347	4954788	97	94.7	3.54	bdl	0.0018	0.065	0.0166	0.0009	0.64	0.96	0.03554	0.013		
YL06-09		Black_Pit	8 09/01/2006	fum	94.5	523589	4952144	0.44	96.9	1.73	0.052	0.0025	0.528	0.0155	0.003	0.56	0.17	0.00244	bdl		
YL06-10		Back_Basin5	8 09/01/2006	fum	92.1	523155	4952043	0.21	94.9	3.39	0.009	0.0030	0.658	0.0210	0.010	0.82	0.22	0.00785	bdl		
YL06-11		Guardian	8 09/01/2006	fum	92.5	523477	4952724	0.56	96.7	2.31	0.082	0.0021	0.386	0.0098	0.004	0.38	0.14	0.00208	bdl	7.43	7.43
YL06-12		Behind_Congress	8 09/01/2006	pool	92.7	523655	4952727	0.22	96.0	2.33	0.024	0.0033	0.531	0.0234	0.006	0.90	0.22	0.00471	bdl		
YL07-01	Gas_Vents_Norris_Canyon_Rd		10 09/12/2007	fum	91.1	535328	4951009	1.8	96.6	2.40	bdl	0.0052	0.025	0.0135	0.0005	0.56	0.36	0.00188	bdl		
YL07-02	Sulphur_Caldron2		14 09/12/2007	fum	98.2	544961	4941790	11	99.4	0.24	bdl	0.0021	0.142	0.0030	0.0008	0.20	0.028	bdl	bdl	15.28	15.29
YL07-03	Mud_Geyser		14 09/12/2007	fum	114.7	545055	4941202	9.5	99.5	0.14	0.005	0.0020	0.074	0.0029	0.0003	0.19	0.037	0.00004	bdl	16.48	16.49
YL07-04	Behind_Inkpot		2 09/13/2007	fum	92.4	545106	4956992	2.3	90.4	3.33	1.108	0.0009	1.931	0.0010	0.005	0.20	3.0	0.00374	bdl	4.91	4.91
YL07-05	Washburn		2 09/13/2007	fum	93.2	545135	4957173	1.7	83.0	2.58	1.093	0.0007	4.64	0.0089	0.012	0.43	8.2	0.01062	bdl	4.78	4.78
YL07-06	Pocket_Basin		3 09/14/2007	fum	93.7	513979	4934350	0.15	95.7	1.99	bdl	0.0050	0.341	0.0430	0.008	1.6	0.35	0.00236	bdl	2.95	2.95
YL07-09	Guardian		8 09/15/2007	fum	92.1	523477	4952724	0.32	96.5	2.02	0.086	0.0032	0.703	0.0107	0.003	0.45	0.21	0.00083	bdl		
YL07-10	Steamvalve		8 09/15/2007	pool	68.8	523494	4952561	87	97.0	0.60	bdl	0.0030	0.545	0.0414	0.0010	1.6	0.20	0.00081	0.003	8.76	8.79
YL07-11	Bison_Flat		8 09/15/2007	fum	92.1	523548	4953837	1.3	95.4	3.82	bdl	0.0043	0.151	0.0084	0.001	0.33	0.30	0.00665	bdl		
YL07-12	Roaring_Mountain2		6 09/16/2007	fum	92.4	520703	4958588	0.46	97.5	1.76	bdl	0.0097	0.147	0.0135	0.002	0.54	0.044	0.00037	bdl		
YL07-13	Mud_Geyser		14 09/16/2007	fum	nm	545055	4941202	8.7	99.5	0.15	0.002	0.0021	0.079	0.0033	0.0009	0.21	0.041	0.00007	bdl		
YL07-14	Fountain_Paint_Pot		3 09/17/2007	fum	92.0	515376	4933087	0.22	95.7	0.35	0.047	0.0056	0.008	0.0762	0.005	2.9	0.18	0.00022	bdl	6.06	6.07
YL07-15	Beryl_Spring		18 09/17/2007	fum	92.5	520077	4947298	0.79	98.7	0.80	bdl	0.0015	0.195	0.0059	0.002	0.26	0.026	0.00007	bdl	12.19	12.22
YL07-17	Crater_Hills		1 09/18/2007	fum	90.9	541392	4944637	3.0	98.4	1.27	bdl	0.0026	0.016	0.0047	0.010	0.25	0.056	0.00004	bdl	10.37	10.37
YL07-18.1	Devils_Den		1 09/18/2007	¹ fum	23.7	549070	4971350	86	78.1	1.11	bdl	bdl	0.011	0.2134	2.60	17.6	0.29	0.01075	0.007		
YL07-18.2	Devils_Den		1 09/18/2007	¹ fum	23.7	549070	4971350	74	79.2	1.03	bdl	bdl	0.001	0.2026	2.40	16.9	0.27	0.01034	0.008		
YL08-02	Steamboat_Point		11 09/17/2008	fum	93.4	555848	4930907	0.21	91.9	3.46	0.724	0.0239	0.441	0.0440	0.002	1.6	1.8	0.00484	bdl	0.76	0.76
YL08-03	Potts_Basin1		13 09/17/2008	pool	68.8	533421	4919761	81	94.2	bdl	bdl	0.0037	0.001	0.1148	0.42	4.3	0.91	0.00134	0.002		
YL08-04	Potts_Basin2		13 09/17/2008	pool	87.5	533505	4919689	44	92.9	bdl	bdl	0.0007	0.003	0.1601	0.36	6.3	0.23	bdl	0.012	4.35	4.73
YL08-04B	Potts_Basin2A		13 09/17/2008	pool	87.5	533505	4919689	80	88.5	bdl	bdl	0.0013	0.002	0.2448	0.74	10.2	0.32	0.00053	0.003		
YL08-05	Potts_Basin3		13 09/17/2008	pool	45.3	533504	4919547	98	88.5	0.003	bdl	0.0079	0.026	0.1806	1.30	8.2	1.8	0.00278	0.003		
YL08-07B	Snake_River_HS		1 09/18/2008	pool	81.4	527133	4887672	87	53.2	bdl	bdl	0.0424	0.012	1.0219	0.68	44.7	0.38	0.00357	0.01	0.81	0.80
YL08-08	Conoco		15 09/18/2008	fum	93.5	513195	4922978	0.15	95.9	1.09	bdl	0.0025	0.119	0.0671	0.005	2.3	0.55	0.00143	0.03		
YL08-09	Forest_Springs1		5 09/19/2008	fry	91.0	541730	4950841	3.5	98.6	0.96	bdl	0.0021	0.212	0.0031	bdl	0.14	0.079	0.00055	bdl	11.65	11.65
YL08-10	Forest_Springs2		5 09/19/2008	fry	87.6	541609	4951154	3.8	98.6	1.01	bdl	0.0018	0.191	0.0029	bdl	0.13	0.073	0.00042	bdl	11.93	11.93
YL08-11	Ochre_Spring		1 09/19/2008	fum	91.7	547154	4939408	2.5	98.8	0.15	bdl	0.0024	0.162	0.0155	0.0002	0.66	0.20	0.00018	0.002	12.17	12.19
YL08-12	Poison_Spring		4 09/20/2008	pool	39.3	522453	4979039	90	96.1	0.03	bdl	0.0051	bdl	0.0669	0.22	3.5	0.073	0.00276	bdl	7.71	7.74
YL08-13	Amphitheater_Springs		6 09/20/2008	fry	88.3	521782	4960436	1.8	85.6	2.88	bdl	0.0031	0.370	0.1412	0.28	10.6	0.052	0.00118	bdl		
YL08-14	Obsidian_Pool_fry		14 09/21/2008	fry	90.2	544411	4939629	11	99.4	0.16	0.0004	0.0023	0.107	0.0037	0.0003	0.24	0.044	0.00002	bdl	16.28	16.28
YL08-14B	Obsidian_Pool_fry		14 09/21/2008	fry	90.2	544411	4939629	10	99.4	0.15	0.0019	0.0028	0.116	0.0041	0.0005	0.26	0.044	bdl	bdl		
YL08-15	Obsidian_Pool		14 09/21/2008	pool	89.2	544530	4939794	9.2	98.9	0.11	bdl	0.0020	0.094	0.0144	0.077	0.79	0.036	0.00003	bdl		
YL08-16	Back_Basin6		8 09/21/2008	fum	93.7	523119	4952036	0.11	94.5	2.80	bdl	0.0038	0.851	0.0458	0.013	1.6	0.22	0.00132	bdl	7.28	7.30
YL08-17	Steamvalve		8 09/21/2008	pool	71.4	523494	4952561	84	96.0	0.43	bdl	0.0029	0.481	0.0701	0.010	2.8	0.18	0.00103	0.002		
YL08-18	Brimstone1		9 09/25/2008	pool	6.6	562143	4915346	75	99.0	0.70	0.0015	0.0104	0.007	0.0066	0.0003	0.23	0.075	0.00080	bdl	3.03	3.03
YL08-19	Brimstone2		9 09/25/2008	pool	16.3	562447	4914975	80	98.9	0.58	bdl	0.0113	0.00003	0.0105	0.002	0.37	0.093	0.00083	bdl	2.98	2.99
YL08-20	Brimstone3		9 09/25/2008	pool	nm	562134	4915341	83	99.0	0.64	bdl	0.0106	0.00008	0.0081	0.006	0.24	0.076	0.00081	bdl		
YL09-01	Conoco		15 09/08/2009	fum	93.3	513206	4922948	0.08	94.3	1.61	bdl	0.0038	0.116	0.0898	0.009	3.1	0.70	0.00357	bdl	6.05	6.30
YL09-02	Black_Sands1		15 09/08/2009	pool	90.0	511542	4923259	0.91	97.8	0.007	0.022	0.0012	0.015	0.0446	0.220	1.6	0.25	0.00041	bdl	7.58	8.10
YL09-03A	Gas_Vents_Norris_Canyon_Rd		10 09/08/2009	fum	92.9	535321	4951008	1.7	96.8	2.16	bdl	0.0051	0.061	0.0151	0.0003	0.64	0.34	0.00239	bdl	4.53	4.55
YL09-03B	Gas_Vents_Norris_Canyon_Rd		10 09/08/2009	fum	92.9	535321	4951008	1.7	96.8	2.08	bdl	0.0054	0.046	0.0170	0.0007	0.72	0.36	0.00236	0.011		
YL09-04	Frying_Pan_Spring		17 09/09/2009	fry	92.3	521972	4955470	1.6	98.1	1.09	0.006	0.0051	0.344	0.0088	0.002	0.35	0.086	0.00027	bdl	5.60	5.65
YL09-05	Heart_Middle		16 09/11/2009	pool	89.9	538455	4905116	3.9	96.6	0.04	0.005	0.0048	0.002	0.0751	0.130	2.3	0.63	0.00217	0.174	1.20	1.21
YL09-06	Heart_Fissure		16 09/11/2009	fum	92.9	538183	4905810	0.18	95.5	0.75	0.072	0.0144	0.100	0.0750	0.009	2.2	1.2	0.00517	bdl	1.14	1.14
YL09-07B	Heart_Lower		16 09/11/2009	pool	84.0	539343	4904383	62	64.8	0.02	bdl	0.0184	0.005	0.4226	6.70	27.1	1.00	0.00416	0.011		
YL09-08	Heart_Rustic		16 09/11/2009	fum	93.0	539330	4903255	0.60	83.1	0.66	0.366	0.0667	0.023	0.3101	0.039	10.5	4.5	0.01532	0.4	1.09	1.09
YL09-09	Heart_North		16 09/12/2009	fum	92.9	537947	4906671	0.30	93.2	0.61	0.030	0.0201	0.076	0.1004	bdl	3.7	2.1	0.00888	0.184	1.81	1.81
YL09-10	Heart_White_Gulch		16 09/12/2009	fum	92.7	537259	4906392	0.38	93.7	0.64	bdl	0.0130									

Table 2. Sample collection parameters and major and trace chemical data for gas samples collected within and around Yellowstone National Park, Wyoming during 2003 through 2009.—Continued

Sample number	Ne2022	Ne2122	Ar3836	Ar4036	F ⁴ He	HeNe_Air	⁴ He/ ⁴⁰ Ar*	¹³ C-CO ₂ per mil	¹³ C-CH ₄ per mil	³⁴ S-H ₂ S per mil	CO ₂ - ³ He	δD _s per mil	δ ¹⁸ O _s per mil	N ₂ /Ar	YNP Thermal Features Database
YL03-01A	9.952	0.029		284		32					2.08E+09	-173	-21.0	40.0	
YL03-02A	9.888	0.029		287		84		-3.2			2.17E+09	-175	-22.7	39.3	Fumarole
YL03-03A								-3.4				-178	-21.1	35.2	
YL03-04A								-3.4						38.9	
YL03-05B	9.919	0.029		291		5					3.50E+09	-172	-20.2	41.6	
YL03-06B								-3.0						40.2	Green Dragon Spring
YL03-07	9.992	0.029		284		10					7.83E+09	-167	-20.2	40.0	Son of Green Dragon Spring
YL03-08								-2.7						39.1	Dishwater Spring
YL03-09B	10.01	bdl		278		53				-1.0	5.02E+09	-178	-21.1	41.5	GGCGN073
YL03-10B	10.02	0.030		281		29		-4.7			5.81E+09	-168	-20.8	39.4	Black Growler
YL03-11B								-2.7						41.1	Black Pit Spring
YL03-12A								-3.3				-171	-20.8	34.9	
YL03-13A	10.07	0.030		287		124		-3.0		0.2	3.45E+09	-167	-19.8	39.8	
YL03-14B	9.761	bdl		292		186		-4.3			3.37E+10			31.3	GTSANN003
YL03-15A	9.905	0.029		299		220		-3.0		-1.2	1.39E+09			39.1	
YL03-16A	10.01	bdl		325		740					2.89E+09			41.3	
YL03-17A		na		294		19		-3.6			4.02E+09	-171	-22.0	38.1	
YL03-18A								-4.0						38.4	
YL03-19A	9.987	0.029		292		95		-4.9			1.69E+09	-163	-20.6	38.1	
YL03-20								-4.9						42.0	
YL03-21A	9.968	0.029		302		95		-4.8			1.56E+09	-162	-21.7	39.0	
YL04-01								-3.7						40.1	Black Pit Spring
YL04-02								-2.0						39.3	
YL04-03								-1.9						40.9	
YL04-04	10.31			312		1021		-3.5			3.24E+09	-159	-19.3	42.6	
YL04-05	10.10			293		100		-3.5			4.04E+09	-174	-23.3	38.7	
YL04-06	10.36			289		159		-2.6			1.59E+10			43.3	
YL04-07								-3.2				-176	-23.4	41.9	
YL04-08								-4.1				-174	-22.4	40.8	
YL04-09	9.947			285		48		-2.7			5.78E+09			36.0	NBBNN032
YL04-10								-2.5						66.8	Green Dragon Spring
YL04-11								-3.4				-175	-23.4	38.8	
YL04-12	10.36			299		635		-3.1			3.81E+09	-169	-22.0	39.0	
YL04-13	9.896			292		205		-2.6			1.88E+09			40.7	
YL04-14	9.871			297		20		-4.1			8.47E+09	-171	-20.7	58.0	
YL04-15	9.855			294		1.3		-2.3			1.46E+11			41.7	
YL04-17	10.46			286		101		-3.0			2.81E+09			41.5	
YL04-19	10.17			345		714		-3.2			2.87E+09	-164	-21.3	43.2	GSSGNN060
YL04-20								-3.2				-149	-18.8	42.4	GSSGNN060
YL04-21	9.978			314				-2.9			2.84E+09	-162	-21.6	39.4	GSSGNN076
YL04-22	10.07			345							4.79E+09			42.7	
YL05-01	10.50			335		2106		-3.8			3.40E+09	-163	-21.7	36.5	Black Pit Spring
YL05-02								-4.8						29.3	GTSANN003
YL05-03								-3.8				-143	-16.3	37.1	NMCNN036
YL05-04	11.40			383		2476		-3.6			3.74E+09	-163	-22.0	43.3	GGCGFM002
YL05-05								-4.6				-166	-22.1	33.7	
YL05-06	10.40			301		148					4.65E+09	-162	-20.1	29.5	
YL05-07								-3.7						35.2	
YL05-08								-3.9				-161	-20.7	34.9	Black Growler
YL05-09								-3.4				-166	-21.8	36.6	
YL05-10	10.10			329		1533		-3.2			3.44E+09	-164	-20.5	37.4	
YL05-11								-4.1						34.0	GCPNN006
YL05-12	11.30			397		1441		-2.7			2.24E+09			47.1	
YL05-13	10.60			606		4354		-2.9			2.08E+09			60.0	
YL05-13A								-2.9						61.9	
YL05-14	10.10			480		9832		-4.2			3.65E+09	-155	-20.1	34.7	
YL05-15								-4.4						38.4	Narrow Gauge Spring and Terrace
YL05-17A	10.30			344		722					2.35E+09	-171	-22.2	34.5	
YL05-17B														35.6	
YL05-18A								-3.2				-164	-21.4	40.6	GGCGFM002
YL05-18B								-3.2				-160	-22.2	43.1	GGCGFM002
YL05-18C								-3.2						33.6	GGCGFM002
YL05-18D								-3.2						41.0	GGCGFM002
YL06-01A	10.08	0.036		418		12006	795	² -4.2			1.51E+09	-148	-15.7	33.5	
YL06-02	9.925	0.029		367		1961	162	² -3.8			1.79E+09			38.5	

Table 2. Sample collection parameters and major and trace chemical data for gas samples collected within and around Yellowstone National Park, Wyoming during 2003 through 2009.—Continued

Sample number	Ne2022	Ne2122	Ar3836	Ar4036	F ⁴ He	HeNe_Air	⁴ He/ ⁴⁰ Ar*	¹³ C-CO ₂ per mil	¹³ C-CH ₄ per mil	³⁴ S-H ₂ S per mil	CO ₂ - ³ He	δD _s per mil	δ ¹⁸ O _s per mil	N ₂ /Ar	YNP Thermal Features Database
YL06-03								² -4.0						31.0	SCANN196
YL06-04	10.12	0.036		466		12634	1447	² -3.9			1.61E+09	-159	-18.6	25.1	
YL06-05								² -3.7						40.4	
YL06-06	10.13	0.031		369		5002	313	² -4.3			2.58E+09			33.4	
YL06-07	10.56	0.030		287		48		² -4.2			4.94E+09	-158	-17.5	78.5	
YL06-08								² -4.0						38.7	
YL06-09								-3.7				-159	-21.2	36.2	Black Pit Spring
YL06-10														39.0	
YL06-11	10.02	0.027		315		1321	13	-3.5			4.51E+09	-168	-21.4	38.8	Guardian Geyser
YL06-12								-4.1						38.6	
YL07-01								-2.8						41.1	
YL07-02	10.35	0.031	0.220	531	2457	3543	1.7	-2.7			2.23E+09			65.7	
YL07-03	10.47	0.031	0.183	593	2803	3924	1.6	-2.8			2.21E+09			66.2	
YL07-04	10.04	0.030	0.199	332	504	1495	2.3	-3.4			1.48E+10			202.0	WHSNN014
YL07-05	9.768	0.030	0.208	403	2497	3767	3.9	-5.0			1.69E+10			47.8	
YL07-06	9.873	0.030	0.217	298	138	438	10.7				4.60E+09			37.2	
YL07-09								-3.5						42.1	Guardian Geyser
YL07-10	9.916	0.029	0.199	303	166	285	3.7	-3.1			2.62E+09			39.4	Steam Valve Spring
YL07-11								-2.9						39.5	
YL07-12								-4.3						39.6	
YL07-13								-2.9						64.5	
YL07-14	9.904	0.030	0.224	308	120	308	1.6	-3.2			2.02E+09			38.4	Fumarole
YL07-15	10.09	0.031	0.183	311	222	377	2.3	-3.4			3.83E+09			44.4	GGCGNN073
YL07-17	10.11	0.030	0.200	351	801	1354	2.4	-2.9			2.63E+09			52.1	
YL07-18.1								-1.4						82.5	
YL07-18.2														83.3	
YL08-02	9.912	0.029	0.196	325	1328	4525	7.4	-3.6	-45.5		3.62E+09	-148	-19.8	37.0	BSRNN033
YL08-03								0.2	-37.9					37.7	
YL08-04	9.970	0.029	0.186	294	8.5	10		-3.4	-43.6		1.89E+10			39.6	
YL08-04B								-3.0	-43.5					41.5	
YL08-05								0.4	-38.7					45.1	
YL08-07B	9.958	bdl	0.192	296	96	266		-13.3			1.12E+09			43.7	
YL08-08									-28.3			-164	-21.7	33.8	
YL08-09	10.01	0.035	0.191	309	796	2560		-3.0	-23.9		2.94E+09			45.2	
YL08-10	10.04	0.030	0.195	332	726	1641	3.3	-4.1	-24.3		3.24E+09			44.8	
YL08-11	9.921	0.031	0.194	317	350	563	2.7	-2.4	-33.6		2.40E+09	-161	-23.5	42.6	Ochre Spring
YL08-12	9.848	0.030	0.198	303	160	218	3.6	-3.3	-44.4		1.75E+09			52.8	Poison Spring
YL08-13								-4.5						75.2	APTNN011
YL08-14	10.44	0.032	0.192	351	1470	4584	4.4	-2.5	-23.4		1.86E+09			64.9	MVNN003
YL08-14B								-2.5	-23.5					63.4	MVNN003
YL08-15								-2.4	-24.6					54.9	Obsidian Pool
YL08-16	10.04	0.030	0.192	302	240	516	1.6				2.43E+09	-162	-19.8	34.1	
YL08-17								-2.8	-31.8					40.5	Steam Valve Spring
YL08-18	10.09	0.035	0.232	736	8447	21636	3.2	-3.0	-42.8		2.25E+09			34.8	
YL08-19	10.24	0.038	0.190	307	501	308	7.1	-2.9	-46.4		2.10E+09			35.2	
YL08-20								-3.0	-43.3					29.6	
YL09-01	9.858			321	78	21	0.50				2.80E+09	-165	-21.9	35.0	
YL09-02	9.840			318	58	14	0.43	-1.7			7.23E+09			36.5	
YL09-03A	9.752			414	1029	158	1.45	-2.7	-28.2		2.97E+09	-152	-20.2	42.4	
YL09-03B								-2.8	-28.0					42.4	
YL09-04	9.977			425	1070	95	1.37	-3.4	-25.4		2.45E+09			39.8	NMCNN036
YL09-05	9.888			314	124	32	1.13	-4.7	-44.2		1.20E+10			30.5	
YL09-06	9.811			347	525	122	1.68	-3.4	-44.1		4.14E+09			29.3	
YL09-07B								-4.4						64.0	
YL09-08	9.869			335	348	78	1.47		-43.2		8.16E+08			33.7	HLRNN018
YL09-09	9.817			323	415	123	2.55	-3.0	-40.5		1.83E+09	-167	-23.9	37.2	
YL09-10	9.795			316	267	75	2.19	-2.0	-36.8		1.91E+09	-155	-21.8	35.2	
YL09-11	9.812			331	227	59	1.08		-36.5		1.67E+09			36.9	
YL09-12									-43.2					37.5	HLRNN018
YL09-13	10.17			347	31	5	0.10				1.66E+09	-163	-22.0	32.0	
YL09-14														37.5	
YL09-15								-4.0						29.5	GTSANN003
YL09-16	10.14			600	2560	121	1.40	-3.0	-32.4		4.27E+09	-158	-19.0	37.1	
YL09-17	10.41			625	3108	78	1.57	-3.0	-32.5		3.91E+09			37.8	
YL09-18	9.784			374	1136	255	2.40	-3.0	-37.3		2.55E+09			39.9	
MDL															

¹Site is a cold gas seep; listed as a fumarole for simplicity.

²Carbon isotope composition is different from that reported in Werner and others (2008).

typically pools have higher X_g because the steam condenses as it bubbles through the water).

The value for a gas-free sample would approach zero. Our expected accuracy is 10 percent relative; that is, an X_g of 10 should be between 9 and 11 mol percent gas.

CO₂: Mole percent carbon dioxide relative to all other gases (H₂O-free). One-sigma uncertainty is 0.2 mol percent (absolute) based on replicate analysis of individual samples. Uncertainty based solely on counting statistics is less than 0.1 mol percent.

H₂S: Mole percent hydrogen sulfide relative to all other gases (H₂O-free). In samples from 2003 through 2006, sulfate concentrations were not corrected (for the blank), and samples with very low H₂S from those years may have slightly higher reported values than their actual concentrations. One-sigma uncertainty is ~5 percent relative, based on replicate analysis of individual samples.

NH₃: Mole percent ammonia relative to all other gases (H₂O-free). One-sigma uncertainty is 10 percent relative based on replicate analysis of individual samples.

He: Mole percent helium relative to all other gases (H₂O-free). One-sigma uncertainty based on replicate analysis of samples is ~1 percent relative.

H₂: Mole percent hydrogen relative to all other gases (H₂O-free). One-sigma uncertainty based on replicate analysis of samples is ~1 percent relative.

Ar: Mole percent argon relative to all other gases (H₂O-free). One-sigma uncertainty based on replicate analysis of samples is ~1 percent relative.

O₂: Mole percent oxygen relative to all other gases (H₂O-free). Most samples had very little O₂. For samples with low O₂ contents, the one-sigma uncertainty is 50 percent relative, based on replicate analysis of individual samples. Most variability is from small amounts of air entrained during sampling. Samples with more than 0.1 mol percent O₂ have much lower uncertainty, and their values should be accurate to within 5 percent relative.

N₂: Mole percent nitrogen relative to all other gases (H₂O-free). One-sigma uncertainty based on replicate analysis of samples is ~2 percent relative. As with O₂, most variation is due to small variations in entrained air.

CH₄: Mole percent methane relative to all other gases (H₂O-free). One-sigma uncertainty based on replicate analysis of samples is ~1 percent relative.

C₂H₆: Mole percent ethane relative to all other gases (H₂O-free). One-sigma uncertainty based on replicate analysis of samples is ~15 percent relative.

HCl: Mole percent hydrogen chloride relative to all other gases (H₂O-free). In reality, nearly all Cl⁻ in the gas sample is not from HCl-bearing gas, but comes from small droplets of Cl⁻-bearing thermal

water that enter into the gas stream at bubbling pools and frying pans. Samples with high apparent HCl may also have anomalous H₂S by the same process. The one-sigma analytical uncertainty is 5 percent relative, but the random appearance of Cl⁻ (through entrainment of thermal water) within replicate samples implies that reproducibility is low.

R/R_a: ³He/⁴He ratio of sample divided by that in air (1.399x10⁻⁶). One-sigma analytical error is 0.01.

R_c/R_a: ³He/⁴He ratio of sample divided by that in air (1.399x10⁻⁶) and corrected for any air that may have been mixed into the sample.

Ne2022: ²⁰Ne/²²Ne ratio in the gas. One-sigma analytical error is 0.003.

Ne2122: ²¹Ne/²²Ne ratio in the gas. One-sigma analytical error is 0.0001.

Ar3836: ³⁸Ar/³⁶Ar ratio in the gas. One-sigma analytical error is 0.004.

Ar4036: ⁴⁰Ar/³⁶Ar ratio in the gas. The air ratio is 298.6. One sigma uncertainty is 2.

F⁴He: ⁴He/³⁶Ar in sample divided by the same ratio in air.

HeNe_Air: The He/Ne ratio in the sample divided by the same ratio in air.

⁴He/⁴⁰Ar*: Counts of ⁴He divided by the calculated radiogenic ⁴⁰Ar (that is, subtracting that ⁴⁰Ar calculated as derived from air). This value approximates the decay ratio of U, Th, and other elements that produce He daughter products compared with those that produce Ar (that is, K).

δ¹³C-CO₂: The ¹³C/¹²C ratio in CO₂, as normalized by the same ratio in the standard Vienna PeeDee Belemnite (VPDB). Units in per mil. $\delta^{13}\text{C}_{\text{sample}} = \{({}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}) / ({}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}}) - 1\} \times 1000$. Two-sigma uncertainty is 0.2 per mil.

δ¹³C-CH₄: The ¹³C/¹²C ratio in CH₄, as normalized by the same ratio in the standard Vienna PeeDee Belemnite (VPDB). Units in per mil. $\delta^{13}\text{C}_{\text{sample}} = \{({}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}) / ({}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}}) - 1\} \times 1000$. Two-sigma uncertainty is 0.2 per mil.

δ³⁴S-H₂S: The ³⁴S/³²S ratio in H₂S, as normalized by the ³⁴S/³²S ratio in the standard Canyon Diablo Troilite (CDT). Units in per mil. $\delta^{34}\text{S}_{\text{sample}} = \{({}^{34}\text{S}/{}^{32}\text{S}_{\text{sample}}) / ({}^{34}\text{S}/{}^{32}\text{S}_{\text{standard}}) - 1\} \times 1000$. One sigma uncertainty is 0.1 per mil.

CO₂-³He: The molar ratio of CO₂ to ³He in the gas sample. The propagated one-sigma uncertainty is 5 percent relative.

δD_s: The ratio of D/H in steam condensed from the gas sample. Steam was condensed to liquid water in select fumarole and frying pan samples. The value is normalized to the D/H ratio in the standard Vienna Standard Mean Ocean Water (VSMOW). Units are reported in per mil (‰). $\delta\text{D}_{\text{sample}} = \{(\text{D}/\text{H}_{\text{sample}}) / (\text{D}/\text{H}_{\text{standard}}) - 1\} \times 1000$. Analytical uncertainty of 1.0 per mil (2003-8) and 0.3 permil (2009), respectively.

$\delta^{18}\text{O}_g$: The ratio of $^{18}\text{O}/^{16}\text{O}$ in steam condensed from the gas sample. Steam was condensed to liquid water in select fumarole and frying pan samples. The value is normalized to the $^{18}\text{O}/^{16}\text{O}$ ratio in the standard Vienna Standard Mean Ocean Water (VSMOW). Units are reported in per mil (‰). $\delta^{18}\text{O}_{\text{sample}} = \{(^{18}\text{O}/^{16}\text{O} \text{ sample}) / (^{18}\text{O}/^{16}\text{O} \text{ standard}) - 1\} \times 1,000$. Analytical uncertainty is 0.1 per mil.

N_2/Ar : The N_2/Ar ratio in the sample. For comparison, the air ratio is 83.6. The ratio in air-equilibrated meteoric water at 10°C is 37.7 (Wilhelm and others, 1977). Propagated one-sigma uncertainty is 1.4 percent relative.

YNP Thermal Features Database: The name of our sampled feature in the Yellowstone National Park Thermal Features Database (<http://www.rcn.montana.edu/resources/features/features.aspx?nav=11>). We only provide the name if our thermal feature is believed to be precisely the same as that shown in the thermal features database.

Data Formats and Uncertainties: Table 3 Water Analyses

Below we outline the data columns in table 3 and information relevant for interpretation of values and their related uncertainties.

Sample: Alpha-numeric codes begin with YL and are followed by a two-digit year code (03 for 2003, for example), a hyphen, and a sample number for that year, finishing with a W (for water).

Location: Informal name for the sampled feature. The name could be a defined thermal feature or could indicate simply that it was sampled in the same general location. When we sampled an actual thermal feature denoted in the Yellowstone Thermal Features database (<http://www.rcn.montana.edu/resources/features/features.aspx?nav=11>), we list the name of that feature in the “YNP Thermal Features Database” column.

Identical Feature: If the water sample comes from the same feature that was sampled for gas (with the same sample name excepting the “W”), then the answer is YES. If the water sample comes from a nearby feature, the answer is NO. For example, the fumarole sampled as YL07-04 is from a steaming area near Inkpot Spring, whereas YL07-04W came from Inkpot Spring itself. In addition, two water samples were collected from areas where gas was not sampled.

Date: In month/day/year format (mm/dd/yyyy).

Temp: Temperature in degrees Celsius. Temperature can be reproducibly measured to within 0.1°C , but accuracy may be limited to $\sim 0.5^\circ\text{C}$ because of temperature variability within the feature and instrumental variations.

Easting: East-west location in Universal Transverse Mercator (UTM) coordinate system, Zone 12. Datum is NAD83 (nearly identical to WGS84). Units are in meters. Uncertainties are generally ~ 3 m.

Northing: North-south location in Universal Transverse Mercator (UTM) coordinates, Zone 12. Datum is NAD83 (nearly identical to WGS84). Units are in meters. Uncertainties are generally ~ 3 m.

δD_w : The ratio of D/H in the sampled thermal water. The value is normalized to the D/H ratio in the standard Vienna Standard Mean Ocean Water (VSMOW). Units are reported in per mil (‰). $\delta\text{D}_{\text{sample}} = \{(\text{D}/\text{H} \text{ sample}) / (\text{D}/\text{H} \text{ standard}) - 1\} \times 1,000$. Analytical uncertainty of 1.0 per mil (2003-8) and 0.3 per mil (2009), respectively.

$\delta^{18}\text{O}_w$: The ratio of $^{18}\text{O}/^{16}\text{O}$ in the sampled thermal water. The value is normalized to the $^{18}\text{O}/^{16}\text{O}$ ratio in the standard Vienna Standard Mean Ocean Water (VSMOW). Units in per mil (‰). $\delta^{18}\text{O}_{\text{sample}} = \{(^{18}\text{O}/^{16}\text{O} \text{ sample}) / (^{18}\text{O}/^{16}\text{O} \text{ standard}) - 1\} \times 1,000$. Analytical uncertainty of 0.1 per mil.

pH (F): pH as measured in the field. For hot spring waters, we used paper indicator strips with an uncertainty of about 0.5. For cold spring waters pH was measured using a calibrated meter with an uncertainty of about 0.1.

pH (L): pH as measured in the laboratory using a calibrated meter with an uncertainty of about 0.1.

Cond. $\mu\text{S}/\text{cm}$: Specific conductance as measured in the laboratory using a calibrated meter.

Cations: Al, B, Br, Ca, Fe, K, Mg, Na, NH_4^+ , and SiO_2 in mg/l. As, Ba, Cd, Co, Cr, Cs, Cu, Li, Mn, Mo, Ni, Sr, Ti, U, and Zn in $\mu\text{g}/\text{l}$.

Anions: Br, Cl, CO_3^{2-} , F, HCO_3^- , PO_4^{3-} , and SO_4^{2-} in mg/l.

TDS: Total dissolved solids in mg/l.

Cation: Cation totals in meq/l.

Anion: Anion totals in meq/l.

Balance: percentage mismatch between anions and cations.

Results

Bulk Gas Chemistry

Nearly all samples were dominated by CO_2 (table 2), most with more than 90 mol percent on a dry-gas basis (excluding water from steam). Exceptions were a few samples high in atmospheric gases either from air contamination during sampling or from boiling of meteoric water (usually samples with low Xg). The next most abundant gas was N_2 , averaging 3.1 mol percent and with a median of 1.0 percent, followed by H_2S (average of 1.3 mol percent, median of 0.9 percent) (table 4). Gas from a slow-bubbling pool near the Snake River, south of the park (fig. 1) had a very anomalous N_2 content in excess of 44 mol percent.

Table 3. Water chemistry, stable isotope values, and sample collection parameters for waters collected within and around Yellowstone Park, Wyoming, during 2003 through 2009.

[Temperature is reported in degrees Celsius (°C). Analyte concentrations are reported in µg/l or mg/l. Stable isotope values of water are reported in per mil relative to SMOW (δD and δ18O). A blank cell indicates that an analysis was not attempted; bdl is below detection limit. Field pH values (pH F) in bold were determined using a meter; others were determined using indicator paper. Laboratory pH values (pH L) were determined using a meter. Some pH values that were determined using indicator paper, were optimized to correct the charge balance; the optimized pH values are reported in the footnotes.]

Sample number	Location	Identical Feature	Date	Temp	Easting	Northing	δD _w	δ ¹⁸ O _w	pH (F)	pH (L)	Cond.	Al	As	B	Ba	Br	Ca	Cd	Cl	Co	CO ₃	Cr
							per mil	per mil				µS/cm	mg/l	µg/l	mg/l	µg/l	mg/l	µg/l	mg/l	µg/l	mg/l	µg/l
YL03-01W	Lone_Star	No	09/04/2003	94.0	515429	4918413	-145	-15.7	8.0			0.50	1460	4.9	5.09	1.32	1.6		434			
YL03-08W	Dishwater	Yes	09/06/2003	89.4	523384	4952086	-132	-9.1	3.1			1.58	2400	9.3	32.5	1.96	6.1		655			
YL03-09W	Beryl_Spring	No	09/07/2003	93.6	520077	4947298	-145	-14.6	6.6			0.35	2700	7.2	1.68	1.58	4.0		559			
YL03-11W	Black_Pit	Yes	09/07/2003	93.9	523595	4952211	-119	-9.6	6.6			0.18	16	1.7	20.9	0.07	2.2		41.8			
YL03-13W	Nymph_Lake_new_feature	Yes	09/08/2003	93.6	521471	4955495	-144	-15.2	8.1			0.38	3620	6.4	12.5	1.37	3.7		443			
YL03-14W	Terrace_Springs	Yes	09/08/2003	63.3	512184	4944102	-156	-18.6	6.5			0.03	190	1.0	5.27	0.16	20		65.4			
YL03-15W	W_Nymph_Lake_Thermal_Area1	Yes	09/09/2003	82.0	520335	4954609	-118	-6.7	(¹)			6.8	3.1	0.58	107	<0.01	9.6		1.3			
YL03-21W	Smokejumper4	Yes	09/12/2003	92.1	503559	4918096	-137	-15.6	5.3			0.72	bdl	bdl	6.24	<0.01	0.4		1.1			
YL04-AW	Nymph_Lake_new_feature	No gas	05/24/2004	61.0	521471	4955495	-136	-14.3	5.5			0.14		6.4	20.3	1.30	4.1		448			
YL04-06W	Bison_Kill	Yes	09/14/2004	8.5	523471	4954042	-102	-12.4	6.6			0.03		7.3	90.9	0.50	28		370			
YL04-09W	Back_Basin2	Yes	09/15/2004	67.4	522963	4952193	-128	-10.7	3.1 ²			1.30		8.6	29.1	1.90	5.8		605			
YL04-13W	Hundred_Springs_Plain	Yes	09/15/2004	89.1	523113	4953330	-147	-15.6	6.4			0.12		8.3	81.4	1.90	2.1		617			
YL04-16W	Y_River_Spring_near_Tower	No gas	09/16/2004	31.6	548920	4971425	-152	-17.4	5.5			0.10		13.0	59.3	0.32	120		104			
YL05-02W	Terrace_Springs	Yes	09/13/2005	62.3	512184	4944102	-150	-18.9	6.5	8.40	1402	0.04	176	1.0	12.2	0.13	19	0.350	64.8	<0.1		0.5
YL05-03W	Frying_Pan_Spring	Yes	09/15/2005	91.8	521979	4955476	-113	-8.9	1.5 ³	2.02	4810	26	9.0	0.09	75.6	0.10	7.9	2.65	0.30	3.4		8.8
YL05-10W	Nymph_Lake_new_feature	Yes	09/16/2005	93.5	521456	4955507	-135	-15.0	7.0	8.06	1823	0.08	3090	6.5	29.0	1.50	4.2	0.090	478	<0.1		<0.3
⁶ YL05-11W	Chocolate_Pots	Yes	09/16/2005	52.5	520496	4950780	-148	-19.1	5.0	8.47	686	0.16	37	0.5	53.1	0.07	20	0.030	32.5	<0.1		<0.3
YL05-15W	Narrow_Gauge	Yes	09/19/2005	74.8	522880	4979593	-149	-18.3	7.0	7.51	2580	0.03	501	3.4	77.6	0.40	330	<0.02	162	<0.1		<0.3
YL05-17W	Quagmire	Yes	09/21/2005	93.4	515413	4934949	-142	-16.4	8.5	9.34	1563	0.20	1340	4.3	7.22	1.00	1.5	0.360	343	<0.1		<0.3
YL07-04W	Behind_Inkpot	No	09/13/2007	92.0	545104	4956992	-120	-8.1	5.0			3800	0.25	0.2	22.0	52.8	<0.01	44		0.20		
YL07-10W	Steamvalve	Yes	09/15/2007	68.8	523494	4952561			3.5			2.20	0.6	5.0	26.3	0.80	2.4	<3	249	<0.4		<3
YL07-16W	Beryl_Spring	No	09/17/2007	88.9	520077	4947298			6.0			0.25	2.4	8.9	19.4	1.70	5.3	<3	575	<0.4		<3
YL08-03W	Potts_Basin1	Yes	09/17/2008	68.8	533421	4919761	-124	-8.9	6.0			0.02	947	1.7	1.59	0.34	0.29	4.52	140	4.5		2.9
YL08-07W	Snake_River_HS	Yes	09/18/2008	81.4	527133	4887672	-140	-18.4	6.0			<0.01	525	1.7	349	0.40	56	2.34	150	<0.001		1.0
YL08-12W	Poison_Spring	Yes	09/20/2008	39.3	522453	4979039	-146	-18.0	6.0			0.01	560	3.6	62.7	0.38	315	2.31	160	<0.001		4.3
YL08-15W	Obsidian_Pool	Yes	09/21/2008	89.2	544530	4939794	-132	-13.9	5.0			0.77	319	6.2	38.8	0.68	8.8	1.33	250	0.45		0.9
YL08-18W	Brimstone1	Yes	09/25/2008	6.6	562143	4915346	-146	-23.9	3.0 ⁴			130	24.6	0.02	7.95	0.0005	169	0.45	0.56	0.56		135
YL08-19W	Brimstone2	Yes	09/25/2008	16.3	562447	4914975	-139	-21.7	2.0			23	6.2	<0.02	8.72	0.01	53	<0.001	0.29	0.77		44
YL08-20W	Brimstone3	Yes	09/25/2008	~13	562134	4915341	-140	-22.3	1.5 ⁵			69	8.6	0.01	12.4	0.0005	96	<0.001	2.00	0.65		140
YL09-05W	Heart_Middle	Yes	09/11/2009	85.8	538455	4905116			7.72	8.02	1822	0.34	1230	3.9	<5	0.88	0.9	5.80	300	<5	2.1	<25
YL09-18W	Pelican_Creek_Trail	Yes	09/16/2009	6.7	557027	4935598	-135	-17.5	4.97	4.83	418	8.0	2.9	<0.02	51.0	0.06	30	<2	0.68	<2		<10

¹pH for YL03-15 not measured and charge balance optimized by assuming a pH = 2.0.

²YL04-09 charge balance optimized by assuming a pH of 2.5.

³YL05-03 charge balance optimized by assuming a pH of 1.82.

⁴YL08-18 charge balance optimized by assuming a pH of 2.1.

⁵YL08-20 charge balance optimized by assuming a pH of 1.75.

⁶Sample YL05-11 likely lost CO₂ to degassing.

Table 3. Water chemistry, stable isotope values, and sample collection parameters for waters collected within and around Yellowstone Park, Wyoming, during 2003 through 2009.—Continued

Sample number	Cs µg/l	Cu µg/l	F mg/l	Fe mg/l	HCO ₃ mg/l	K mg/l	Li µg/l	Mg mg/l	Mn µg/l	Mo µg/l	Na mg/l	Ni µg/l	NH ₄ mg/l	PO ₄ mg/l	Rb µg/l	SiO ₂ mg/l	SO ₄ mg/l	Sr µg/l	Ti µg/l	U µg/l	Zn µg/l	TDS mg/l	Anion meq/l	Cation meq/l	Balance
YL03-01W			16.2	bdl	165	16	2600	0.014	6.1	13	350			<0.01	163	250	25	21		0.042	4.1	1100	16.4	15.9	-3%
YL03-08W			4.7	0.057	0	54	5700	0.109	198	63	370			<0.01	559	430	132	25		0.057	9.2	1680	21.5	19.7	-9%
YL03-09W			18.7	bdl	108	19	5800	0.020	23	134	400			<0.01	363	250	72	8.3		bdl	20	1340	20.1	18.8	-7%
YL03-11W			2.2	bdl	27	15	680	0.183	60	8.1	100			<0.01	111	170	186	10		0.012	6.4	520	5.6	5.0	-11%
YL03-13W			11.8	bdl	126	41	3300	0.035	33	270	290			<0.01	364	490	30	14		0.340	5.2	1320	15.9	14.5	-9%
YL03-14W			7.35	bdl	788	29	660	0.862	235	41	280			<0.01	183	140	12	40		8.800	6.9	554	15.4	14.1	-9%
YL03-15W			0.39	1.54	0	26	55	2.75	538	0.76	33			<0.01	150	300	663	32		1.300	54	1050	13.8	13.7	-1%
YL03-21W			3.59	bdl	45	11	50	0.026	7.0	0.16	40			<0.01	67	230	54	1.4		bdl	3.9	341	2.1	2.2	4%
YL04-AW			7.20	0.193	52	43	3500	0.267	146		250			<0.01	333	380	71	14		7.200		1220	15.3	12.6	-20%
YL04-06W			4.40	0.259	343	75	2700	3.78	323		370			<0.01	373	35	161	449		1.500		1060	19.6	20.0	2%
YL04-09W			5.40	0.071	0	33	5000	0.074	26		290			<0.01	339	310	117	16		0.024		1390	19.8	17.9	-10%
YL04-13W			5.30	bdl	18	64	5600	0.017	6.2		280			<0.01	547	410	43	12		bdl		1430	18.9	14.7	-25%
YL04-16W			2.38	0.211	352	43	910	23.0	130		91			<0.01	130	80	272	963		bdl		752	14.5	13.1	-10%
YL05-02W	30.9	2.9	7.36	0.440	787	32	710	0.906	238	40	280	<30		<0.01	174	140	11	41	22	8.5	27	558	15.4	14.2	-8%
YL05-03W	10.1	1.9	0.30	22.7	0	12	37	3.69	310	0.20	12	<30		<0.01	65.4	140	957	62	74	0.15	68	1190	19.9	20.8	4%
YL05-10W	293	3.0	7.60	0.390	75	39	3800	0.222	109	30	280	<30		<0.01	321	400	41	16	66	0.05	6.8	1260	16.1	13.9	-14%
⁶ YL05-11W	65.7	1.2	4.39	5.57	270	22	800	2.02	1480	8.7	120	<30		<0.01	128	100	25	70	14	0.73	6.1	333	6.1	7.2	17%
YL05-15W	209	1.2	3.10	1.40	902	52	1600	67.2	9.0	bdl	120	<30		<0.01	293	49	556	1930	7.0	<0.006	6.1	1350	31.1	28.8	-8%
YL05-17W	513	3.0	31.4	0.330	167	9	4000	0.012	bdl	140	250	<30		<0.01	135	200	17	4.2	31	<0.006	7.3	861	14.5	11.9	-20%
YL07-04W	2.87		0.40	0.950	23	15	2.3	16.1	329		32		730	0.4	51	150	1830	342				2850	38.4	45.7	17%
YL07-10W	37.0	<20	3.40	0.700	0	16	1900	<0.3	26.9	50	210	<0.7		<0.01	81	760	133	21	25	<0.7	66.0	1390	10.0	10.3	3%
YL07-16W	621	<20	18.8	<0.2	104	23	6800	<0.3	21	111	390	2.0		<0.01	270	320	69	23	19	<0.7	9.0	1420	20.4	18.8	-9%
YL08-03W		0.33	12.0	0.021	366	20	2800	0.024	27	30.8	330	<0.001		0.04		270	140		0.6		17	921	13.5	15.2	12%
YL08-07W		<0.001	5.50	0.006	292	22	1100	8.58	2.8	<0.001	160	<0.001		<0.01		63	44	371			14	512	10.2	11.1	8%
YL08-12W		<0.001	2.80	0.096	655	54	1700	71.0	6.8	<0.001	140	<0.001		<0.01		54	650	2040			<0.001	1450	28.9	29.2	1%
YL08-15W		0.11	15.0	0.541	34	35	1700	1.61	77	166	300	0.33		0.02		320	230	57			16	1170	13.2	14.8	12%
YL08-18W		<0.001	2.00	8.39	0	44	40	99.3	1830	<0.001	78	1.00	0.3		100	2200	2350				<0.001	2830	45.8	43.4	-5%
YL08-19W		<0.001	0.16	2.57	0	14	<0.01	73.0	1320	<0.001	19	0.22		<0.01		74	1100	441			12	1360	22.9	22.5	-2%
YL08-20W		0.11	1.00	16.7	0	34	<0.01	105	1820	<0.001	43	17		0.5		89	2000	1100			36	2460	41.6	42.5	2%
YL09-05W		<5	25.4	<0.005	316	17	6000	<0.005	<5	93	410	<5		<0.01	226	300	153	13				1220	18.3	19.3	6%
YL09-18W		<2	0.53	2.74	70	5	21	20.9	500	<2	14	<2		<0.01	<20	90	172	425			<2	344	4.8	5.0	5%

¹pH for YL03-15 not measured and charge balance optimized by assuming a pH = 2.0.

²YL04-09 charge balance optimized by assuming a pH of 2.5.

³YL05-03 charge balance optimized by assuming a pH of 1.82.

⁴YL08-18 charge balance optimized by assuming a pH of 2.1.

⁵YL08-20 charge balance optimized by assuming a pH of 1.75.

⁶Sample YL05-11 likely lost CO₂ to degassing.

Table 4. Statistical synthesis of individual gas species and radiogenic and stable isotope data for Yellowstone gas samples.

	Units	Minimum	Maximum	Average	1 sigma	Median	No. Samples
Xg (%)		0.05	99.0	23.40	35.7	2.3	130
CO₂	mol%	53.2	99.8	94.2	6.7	96.1	130
H₂S	mol%	0.002	7.6	1.32	1.27	0.87	124
NH₃	mol%	0.0002	1.1	0.082	0.219	0.009	70
He	mol%	0.00003	0.07	0.0056	0.0083	0.0033	128
H₂	mol%	0.00003	6.97	0.538	1.184	0.149	128
Ar	mol%	0.001	1.02	0.072	0.1205	0.0255	130
O₂	mol%	0.0001	6.68	0.235	0.7731	0.0049	124
N₂	mol%	0.1	44.7	3.11	5.59	1.02	130
CH₄	mol%	0.0002	8.18	0.53	0.979	0.212	130
C₂H₆	mol%	0.00001	0.048	0.004	0.008	0.0013	125
HCl	mol%	0.001	0.4	0.04	0.085	0.007	51
R/Ra		0.76	16.48	6.59	3.83	6.11	73
Rc/Ra		0.76	16.49	6.74	3.82	6.24	72
Ar40/36		278	736	349.8	92.1	315.8	73
δ¹³C-CO₂	per mil	-13.3	0.4	-3.4	1.3	-3.2	110
N₂/Ar		25.2	204	44.3	17.9	40	130

Within individual thermal basins, H₂S tended to have higher values in samples with low Xg. Hydrogen averaged 0.5 percent but ranged as high as 6.9 percent and was particularly high at Smokejumper Hot Springs, Washburn Hot Springs, and Hot Spring Basin. Similarly, CH₄ averaged 0.5 percent but reached 8.2 percent at Washburn Hot Springs. NH₃ was notable in samples from Washburn Hot Springs, where concentrations exceeded 1 mol percent, and was > 0.5 percent in a few samples from the Eastern Yellowstone group. Ar values ranged from 0.001 to 1.0 percent, and N₂/Ar ratios were consistent with derivation of these gases primarily from air-saturated meteoric water. All but 12 samples had ratios within the range of 30 to 50; the N₂/Ar of air-saturated water at 10°C should be 37.7, compared with a value of 83.6 in air (Wilhelm and others, 1977). Samples with the highest N₂ and Ar generally were those with the most entrained air. However, O₂ was found in far less abundance than would be appropriate for air-saturated meteoric water (N₂/O₂ = 1.84), probably reflecting reaction of O₂ in groundwater or hydrothermal fluid before mixing/boiling and return to the surface in geothermal gas.

Gas to Steam Ratio (Xg)

The range of gas contents of frying pans (Xg <11 percent) and high-temperature fumaroles (≤14 percent) (table 2) are similar, reflecting boiling and addition of some steam from surface waters. The highest Xg values in high-temperature fumaroles were found consistently at Mud Volcano (fig. 1) and ranged from 10 to 14 percent. The lowest Xg value of any Yellowstone fumarole was 0.05 percent (equivalent to a steam/gas molar ratio of 2,000) in the Norris Back Basin (fig. 1).

Because steam may be lost from gas as it bubbles up through thermal springs, the Xg values of samples from pools are more variable than Xg contents of samples collected at fumaroles or frying pans (table 2). The gas/steam ratios are controlled by temperature, depth of water, and the flux of gas through the feature. Xg ratios for pool samples are generally high (table 2), and most pools with low Xg values are those with temperatures at or close to boiling.

The organic-rich gas vents along the Yellowstone River near Tower Junction (Devils Den) (fig. 1) are very unusual in this dataset but are classified in table 2 as fumaroles for simplicity. The Xg contents of the three samples range from 74 to 89 percent (table 2)—these lukewarm (<30°C) gassy emanations lack the steam that is typically a significant component of true fumarole emissions.

Isotopes

Condensed fumarolic steam had δD_s values varying from ~-180 up to -140 per mil, compared with δD_w values from -160 to -110 per mil for nearby hot spring waters (tables 2, 3; fig. 3). Hot spring waters in this study have δD_w values similar to published values of Yellowstone cold waters (ellipse in fig. 3; Balistrieri and others, 2007; Gemery-Hill and others, 2007; Kharaka and others, 2002; Rye and Truesdell, 1993, 2007) but have slightly higher δ¹⁸O values and plot to the right of the Global Meteoric Water Line. Five cold waters from this study have δD_w and δ¹⁸O_w values ranging from -146 to -102 and -24 to -12 per mil, respectively (table 3).

The δ¹³C values of CO₂ ranged from -13.3 to 0.4 per mil, but the great majority of samples varied only from -5 to -2 (table 2, fig. 4). In fact, 104 of 110 samples fit within that relatively narrow range. The lowest value (by far) of

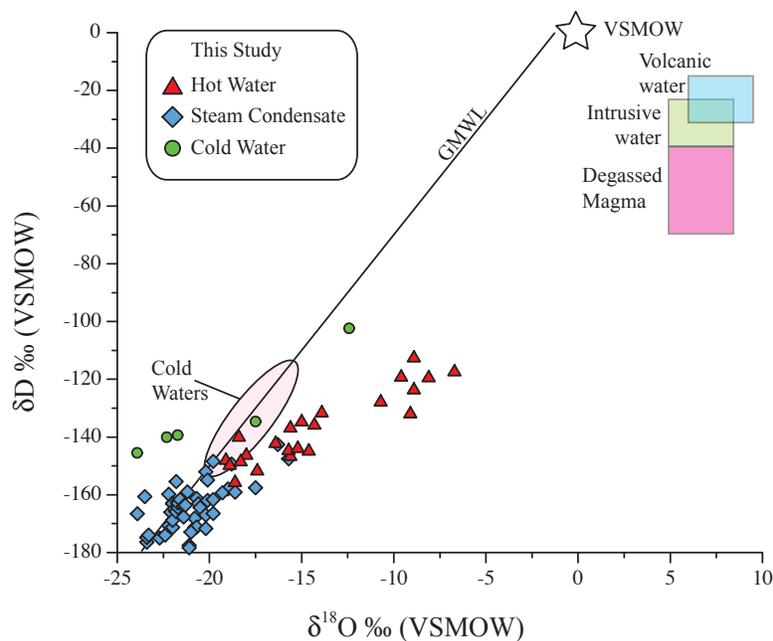


Figure 3. Plot of δD vs. $\delta^{18}O$ relative to Vienna Standard Mean Ocean Water (VSMOW) for condensed steam from selected Yellowstone fumaroles and for hot and cold spring waters from this study. The cold water field (pink ellipse) is from Kharaka and others (2002). Boxes showing the fields for volcanic water, intrusive water, and degassed magma are from Hedenquist and Lowenstern (1994). GMWL = global meteoric water line.

-13.3 per mil was for gas emerging from the Snake River hot spring, our southernmost sample located well outside the Yellowstone Caldera. Such values are more similar to those associated with low-temperature geothermal systems such as those found to the east near Cody, Wyoming (Lorenson and Kvenvolden, 1993; Lorenson and others, 1991). The highest $\delta^{13}C$ -CO₂ values were ≥ 0 per mil from two bubbling pools at Potts Basin.

The spread in helium isotope R_c/R_a (fig. 5) ranged from values below 1.0 at Steamboat Point, Devils Den (R/R_a only), and the Snake River hot spring (table 2) to the highest values

at Mud Volcano (14.98–16.49), which are similar to those found by Craig and others (1978), Kennedy and others (1985), and Werner and Brantley (2003). The locations within the park with the highest values are in the northeastern part of the caldera (Mud Volcano, Forest Springs, and Crater Hills) and the Gibbon River Basins along the northern margin of the caldera. High values around 10 are also known from Shoshone Hot Springs (Hearn and others, 1990), but those springs were not sampled as part of this study. Outside the Yellowstone Caldera, R_c/R_a values >7.0 were found only at sites north of the caldera in the Gibbon River Basins, Norris

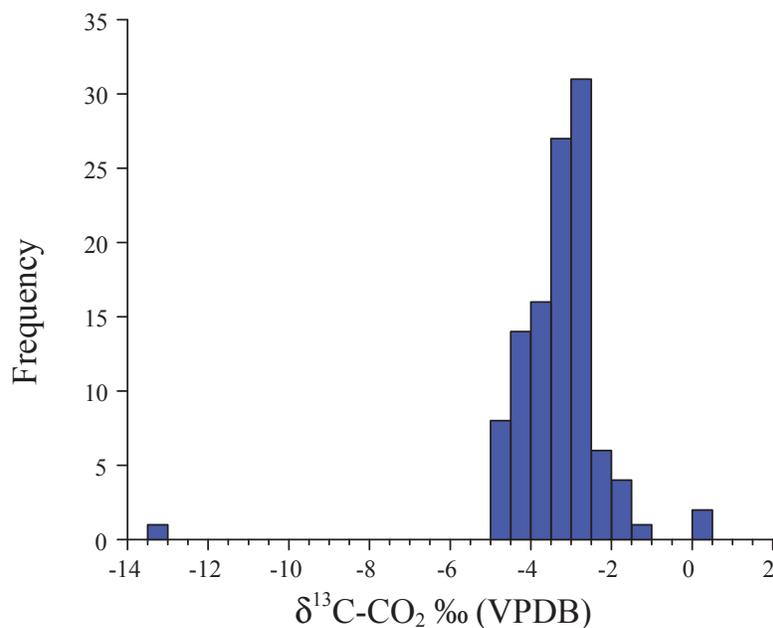


Figure 4. Histogram showing $\delta^{13}C$ values relative to the standard Vienna PeeDee Belemnite (VPDB) for CO₂ in Yellowstone gas: $\delta^{13}C$ values of 104 of the 110 samples are between -2 and -5 per mil. Roughly half of the samples have $\delta^{13}C$ -CO₂ values between -3 and -4 per mil. One sample with an anomalously low $\delta^{13}C$ -CO₂ value of -13.3 per mil is from a hot spring near the Snake River, south of the park boundary.

Geyser Basin, and Mammoth Hot Springs. Not all samples in the Norris Mammoth Corridor, though, yielded high values, as the sample from Roaring Mountain was notably low (see also Kennedy and others, 1985).

Discussion

Water and Steam Isotopes ($\delta^{18}\text{O}$ and δD)

All water and steam samples are very depleted in D and ^{18}O relative to volcanic gas and magma-derived water (Giggenbach, 1992a), consistent with a meteoric origin for the water with relatively minimal (< a few percent) influence of magmatic water (Craig and others, 1956). The hot spring waters have likely exchanged oxygen during water-rock reaction (Craig and others, 1956), which typically produces a positive shift in $\delta^{18}\text{O}_w$ with little or no change in δD_w . The difference in $\delta^{18}\text{O}$ and δD values between seven steam condensates and co-sampled thermal waters (tables 2 and 3) are consistent with fractionation factors expected for boiling at temperatures between 90°C and 110°C (Friedman and O'Neil, 1977; Horita and Wesolowski, 1994). For example, using the equations from Horita and Wesolowski (1994), spring water near Lone Star Geyser, sample YL03-01W ($\delta^{18}\text{O}_w = -15.7$ and $\delta\text{D}_w = -145$), would be in equilibrium at 100°C with steam having an isotopic composition of $\delta^{18}\text{O}_w = -20.6$ and $\delta\text{D}_w = -173$, almost precisely the values observed in fumarolic steam condensate from YL03-01A (table 2).

Gas Chemistry

Different regions had unique gas chemistries (fig. 6). For example, parts of the Norris Geyser Basin were characterized by abundant air-derived gas (N_2 , Ar, O_2), whereas reduced gases (CH_4 , H_2S , H_2) were high at Hot Spring Basin and high H_2S was found at Roaring Mountain. Relative amounts of He, N_2 , and Ar in fumaroles and frying pans are such that virtually all samples plot on a single trend, oriented between air-saturated meteoric water and a He-rich end member (fig. 7). With the exception of slightly elevated N_2 at Washburn Hot Springs, presumably due to breakdown of organic-rich sediments in the mid to shallow crust, there is little evidence for N_2 -rich sources as are common in subduction-zone volcanoes (Giggenbach, 1992b).

Systematics of CH_4 -Ar-He (fig. 8) illustrate that individual thermal areas have a unique character, ranging from Ar-rich (groundwater-derived) to those with diverse CH_4 /He ratios. In helium-rich samples the helium is usually attributed either to deep crustal sources (low R_c/R_a) or mantle sources (high R_c/R_a) (Giggenbach and others, 1993), both of which are present at Yellowstone. Methane, in contrast, is typically attributed to crustal sources (Giggenbach and others, 1993; Lowenstern and Janik, 2003) and when plotted with helium provides a simple method to help discriminate crustal and magmatic endmembers (Chiodini, 2009).

Some geographic areas—for example, Norris (group 8), the Upper Geyser Basin (group 15), and the Gibbon River Basins (group 18)—have narrowly defined CH_4 /He and form

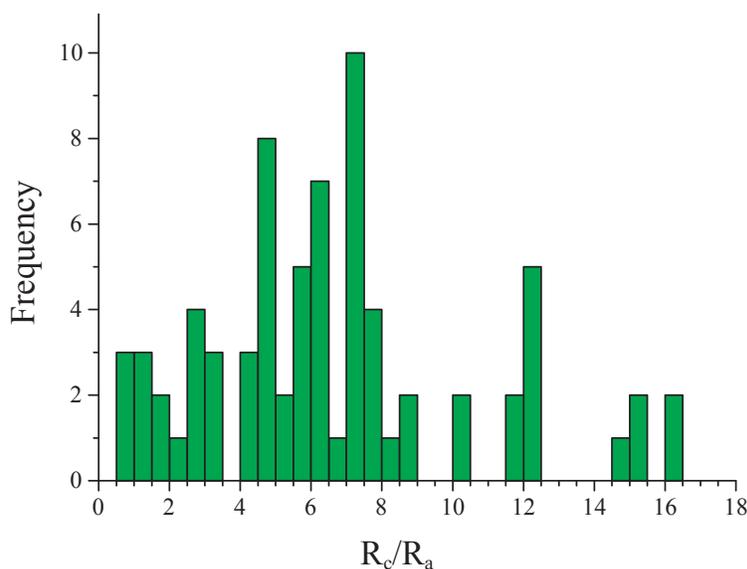


Figure 5. Histogram showing $^3\text{He}/^4\text{He}$ R_c/R_a values for 73 gas samples collected from Yellowstone. Values range from about 0.8 to 16.5. The highest values are from the Mud Volcano area (group 14).

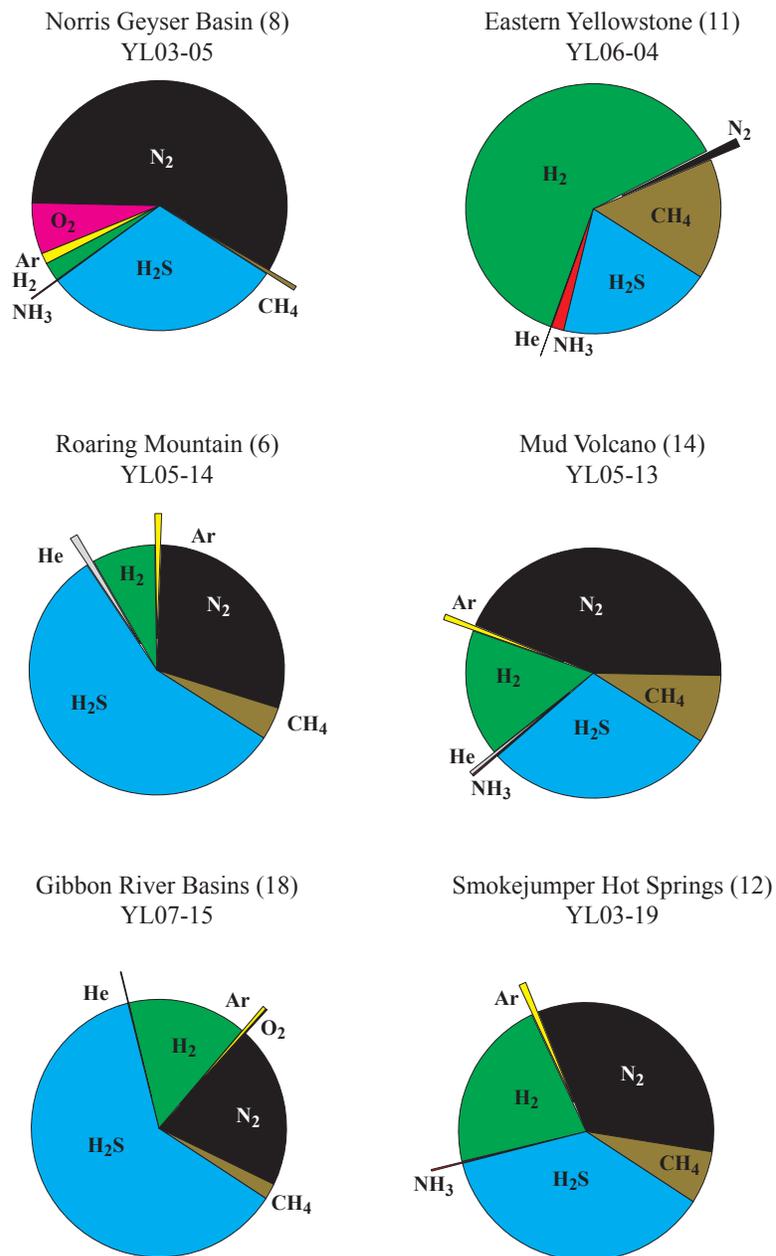


Figure 6. Pie charts demonstrate the differences among gas discharges at Yellowstone. Each section represents that part of the gas fraction after omitting H₂O and CO₂. Very narrow sections are extended for visibility. The Norris Geyser Basin is N₂-rich, consistent with low X_g from steam produced by boiling of meteoric water. Hot Spring Basin (Eastern Yellowstone group) is comparatively rich in reduced gas species such as H₂ and CH₄. Beryl Spring (Gibbon River Basins group) and Roaring Mountain contain a greater proportion of H₂S relative to the other gases. Numbers in parentheses above each chart correspond to the sample groups as defined in table 1.

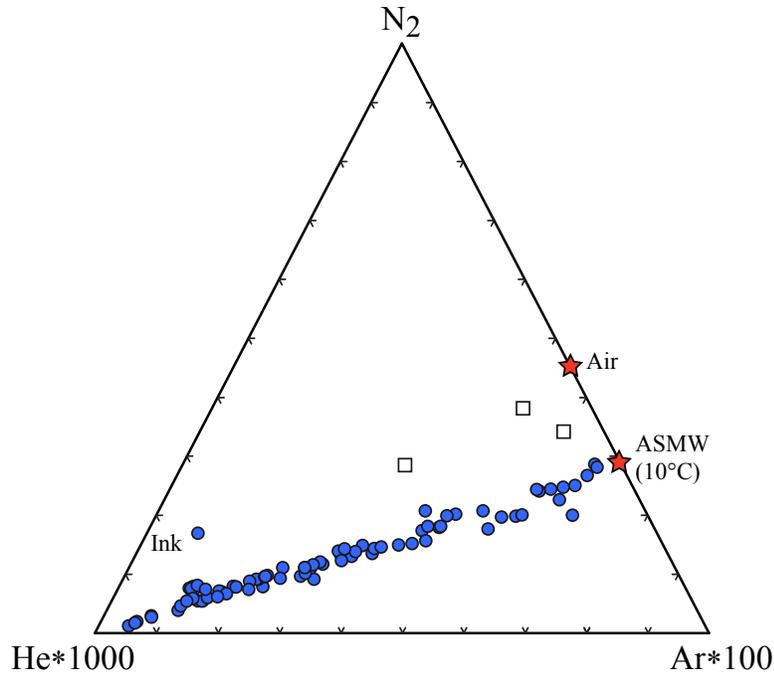


Figure 7. Ternary diagram showing He, N₂, and Ar relations for gas collected from fumaroles and frying pans, which demonstrates that nearly all represent mixtures derived from air-saturated meteoric water with He-rich endmember(s). Squares show three samples that contain some air. Ink is a N₂-rich sample from the Washburn Hot Springs group. ASMW = Air-saturated meteoric water.

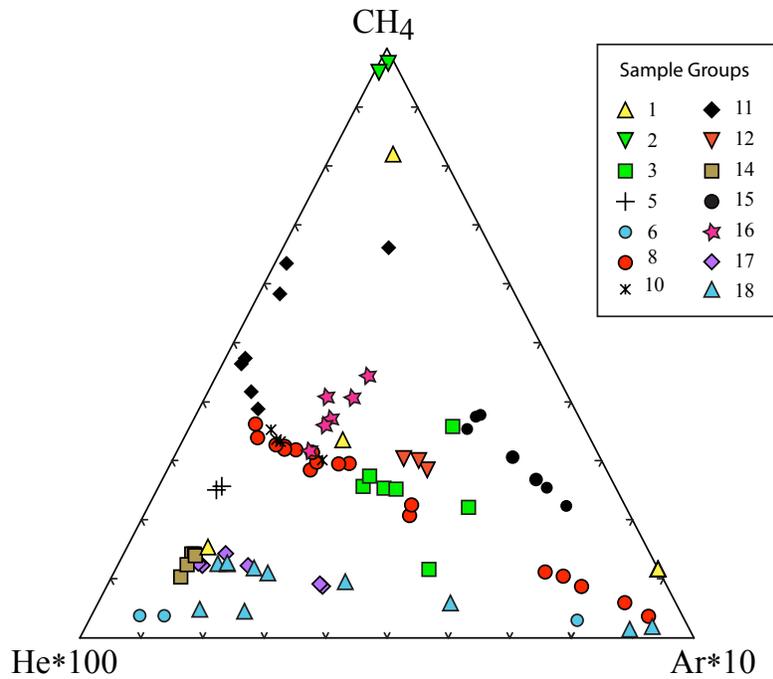


Figure 8. Ternary diagram showing He, CH₄, and Ar relations for gas collected from fumaroles and frying pans, which demonstrates that Yellowstone gases can be discriminated by their CH₄/He ratios, that discrete geographic areas have unique CH₄/He ratios and that most groups form an array of mixtures of magmatic and crustal gases with those derived from boiling of meteoric waters (Ar-endmember). Numbers listed in the legend correspond to the sample groups as defined in table 1.

linear trends from the Ar apex (fig. 8). Interestingly, CH_4/He ratios in some areas that are distant from one another are similar and fall along the same trends. The North of Norris samples (for example, Frying Pan Springs, Nymph Lake, and the West Nymph Lake Thermal Area, group 17) are collinear with gases from the Gibbon River Basins (group 18), ~5 km to the south, and with Mud Volcano (group 14), 25 km to the southeast. Conversely, spatial proximity does not ensure similarity in CH_4/He ratios, as nearby areas have geochemically unique characteristics. CH_4/He ratios for the North of Norris Geyser Basin group are distinct from Norris Geyser Basin itself (fig. 9). Of all the groups, only the Heart Lake, Lower Geyser Basin, and Eastern Yellowstone groups show substantial internal diversity in CH_4/He (fig. 8).

The geochemical distinctions that we observed clearly are not related to the type of thermal feature. Fumaroles, pools, and frying pans from the same thermal basin (for example, Norris Geyser Basin) demonstrate similar gas ratios, such as CH_4/He or CO_2/H_2 . Moreover, water chemistry is not a key factor. At the Norris Geyser Basin, gases that issue from

neutral waters at Hundred Springs Plain have the same CH_4/He ratio as gases from acid, steam-heated waters nearby at “Bison Flat,” along the Gibbon River. Yet neutral waters of the Upper Geyser Basin are distinct from those at Heart Lake or Crater Hills. Gas from acid, steam-heated terrains at Mud Volcano, Smokejumper Hot Springs, and Forest Springs display remarkable internal consistency within groups (fig. 8) but are different from each other and are each readily identifiable by their distinct gas ratios. Only the gases from the carbonate-forming waters at Mammoth Hot Springs and Terrace Springs share some similarity in having high CO_2 and very low He and CH_4 (table 2).

Some authors use methane-to-ethane ratios ($\text{CH}_4/\text{C}_2\text{H}_6$) as the basis for gas geothermometry (Darling, 1998; Tassi and others, 2007), but the strong thermogenic character in some Yellowstone gases (Des Marais and others, 1981) can produce suspicious results. For example, subsurface temperatures calculated for Brimstone Basin (average $\text{CH}_4/\text{C}_2\text{H}_6 = 100$), an area without any discernible geothermal heat flow, would exceed those of Hot Spring Basin (average $\text{CH}_4/\text{C}_2\text{H}_6 = 42$),

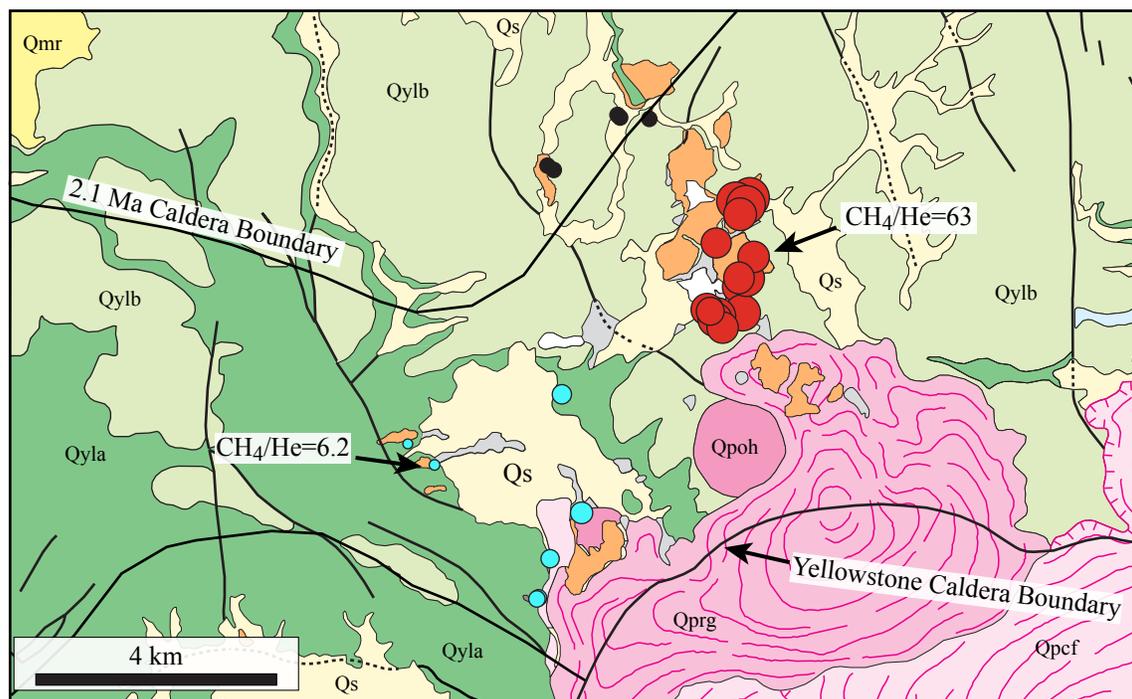


Figure 9. Map (from Christiansen, 2001) of the area around Norris Geyser Basin, showing some of the gas-sample localities plotted as colored dots sized in proportion to the CH_4/He ratio. Norris Geyser Basin samples are red, Gibbon River Basin are blue, and North of Norris Geyser Basin are black. The CH_4/He ratios for two samples, Sylvan_Springs2 and Porcelain_Terrace1 are shown as examples. Ratios in the Norris Geyser Basin are significantly higher than in the two other areas to the north and south. Geological units are Lava Creek Tuff Unit A (Qyla), Lava Creek Tuff Unit B (Qylb), alluvium (Qs), Gibbon River rhyolite flow (Qprg), Gibbon Hill Dome (Qpoh), Solfatara Plateau flow (Qpcf), and Madison River basalt (Qmr). Orange indicates areas of hydrothermal alteration, gray indicates hot spring deposits, white indicates cemented ice-contact deposits, blue is a lake.

seemingly one of the hottest basins at Yellowstone on the basis of other gas geothermometers and geophysical data (Werner and others, 2008). Our findings show that, while $\text{CH}_4/\text{C}_2\text{H}_6$ ratios vary considerably across Yellowstone (table 2, fig. 10), they are generally constrained within individual thermal groups. These discrete trends in figure 10 show that near-surface biological activity or temperature variations exert limited control and instead imply that lithologies and redox conditions in the source region strongly control the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio. Although our $\delta^{13}\text{C}\text{-CH}_4$ analyses only begin in 2008, a plot of those values against $\text{C}_2\text{H}_6/\text{CH}_4$ (fig. 11) indicates that the CH_4 is mainly a mixture of abiotic and thermogenic end members, with the thermogenic signature strongest in features associated with exposures of the Eocene Absaroka Volcanic Supergroup rocks. Apparent trends toward the biogenic box (at Brimstone Basin, Heart Lake, and Potts Basin) may indicate either minor addition or minor removal of isotopically light CH_4 due to near-surface microbial processes.

We note that H_2 concentrations (also used as a geothermometer when normalized to Ar; Giggenbach and Goguel, 1989) and H_2/CO_2 ratios correlate with geography rather than inferred and known subsurface temperatures (White and others, 1975; Fournier, 1989), implying that different areas may have unique oxidation states rather than varying temperatures. For example, figure 7 of Fournier

(1989) shows that chloride-enthalpy relations indicate that Norris and Crater Hills waters rise from the highest temperature geothermal reservoirs. In contrast, hydrogen-argon ratios at Norris (average ratio of 17) and Crater Hills (3.4) are much lower than the hydrogen-rich (seemingly reduced) gases from Eastern Yellowstone (414), Washburn Hot Springs (1,200) and Smokejumper Hot Springs (29).

The distinct gas signatures are most likely related to the lithologies with which subsurface hydrothermal fluids have interacted. Our samples from the Eastern Yellowstone and Washburn Hot Springs groups are enriched in CH_4 and have consistently high CH_4/He (table 2, fig. 8). The Eastern Yellowstone samples from Hot Spring Basin and areas at the eastern edge of Yellowstone Lake emerge where Eocene Absaroka Volcanic Supergroup rocks are found. Units within these rocks are known for their abundant organic carbon and are associated with petroleum seeps such as those found at Rainbow Hot Springs (Love and Good, 1970; Clifton and others, 1990). Terrace Springs, by contrast, emerges from the north wall of the caldera, closer to sedimentary rocks of the Mesozoic/Paleozoic Gallatin Mountains than any other thermal area within the caldera. Gas from Terrace Springs has little CH_4 or H_2S , and instead has high concentrations of CO_2 . In addition, samples from Mud Volcano have low concentrations of CH_4 , and have very high Xg and Rc/Ra values. Lowenstern and Hurwitz

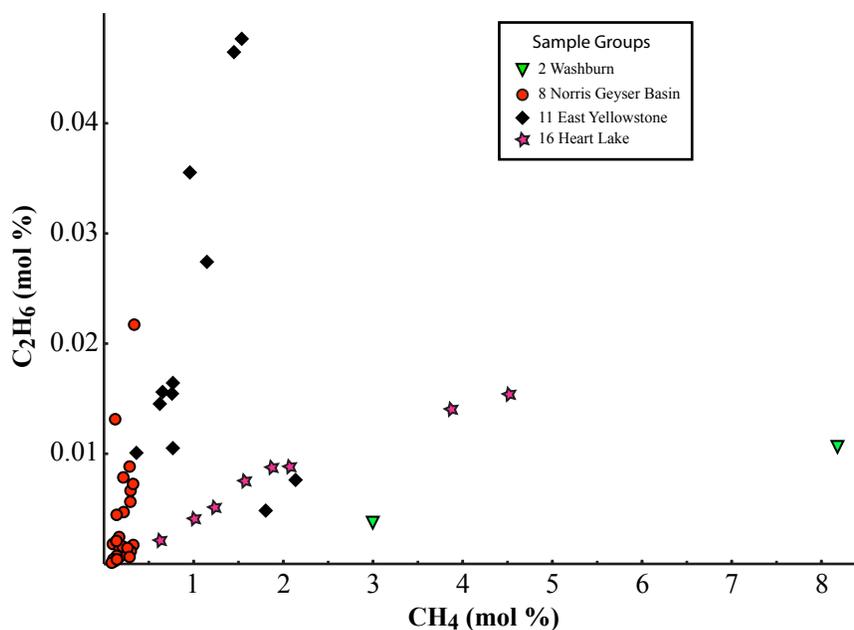


Figure 10. Plot showing mol percent CH_4 versus mol percent C_2H_6 for samples from Eastern Yellowstone, Washburn Hot Springs, Norris Geyser Basin, and Heart Lake (groups 11, 2, 8, and 16, respectively). The discrete linear trends require constant but differing $\text{CH}_4/\text{C}_2\text{H}_6$ ratios in each of these geographic areas.

(2008) concluded that parts of the Yellowstone hydrothermal systems, especially those in acid sulfate terrains such as Mud Volcano, are gas-saturated down to several kilometers depths. The low CH_4 and lack of radiogenic He imply that crustal inputs have less influence on gases in this particular part of the park, potentially because magma is either shallower (Husen and others, 2004), more recently emplaced, or has a more direct connection to the surface.

Summary

We present a dataset containing 130 gas analyses and 31 water analyses collected from thermal areas at Yellowstone from 2003 through 2009. Data are organized into 17 sampling groups plus a group containing miscellaneous samples. Our gas samples show minimal effects by mixing with air and most have N_2/Ar consistent with derivation from air-saturated water. Stable isotope values ($\delta^{18}\text{O}$ and δD) of

waters agree with previous detailed studies that the thermal waters are predominantly derived from meteoric waters. $\delta^{18}\text{O}$ and δD values of condensed steam are 20 to 30 per mil lower than associated thermal waters, consistent with boiling at temperatures between 90°C and 110°C . Isotope values of carbon and helium indicate gases are derived from mixtures of a variety of crustal and magmatic sources. Individual thermal areas have distinct gas signatures that differentiate them from other thermal areas at Yellowstone. We interpret these characteristic gas signatures as indicative of mixing of diverse magmatic, crustal, and meteoric gas sources within the subsurface. Wallrocks influence gas chemistry in some areas, defining local oxidation states, gas concentrations, and gas ratios. Organic species such as CH_4 and C_2H_6 are derived primarily from breakdown of organic-rich sediment, combined with abiogenic reaction of CO_2 and H_2O under geothermal conditions. Trends toward biogenic CH_4 indicate that biological activity may produce a small proportion of the gas flowing from Yellowstone hot springs and fumaroles.

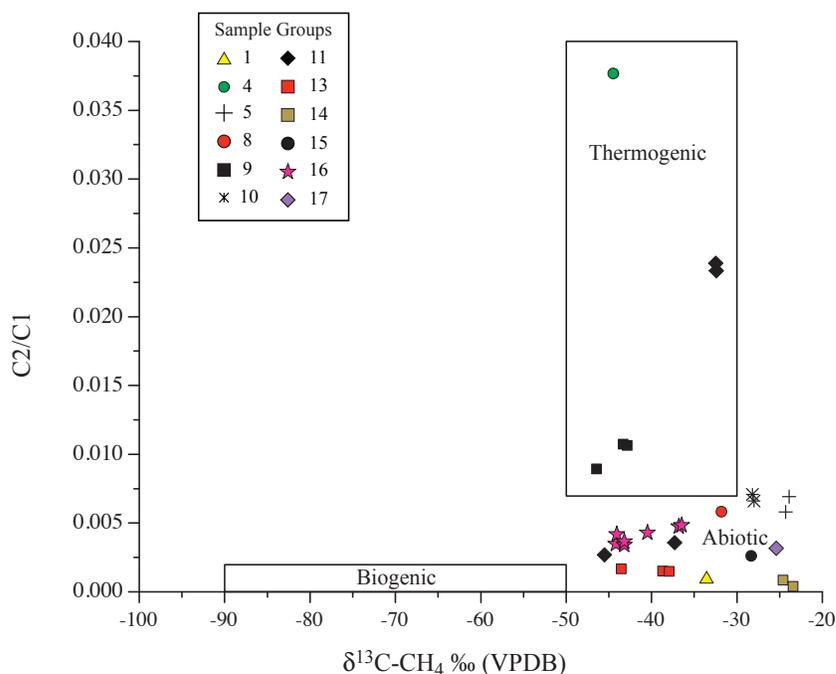


Figure 11. Plot showing the ethane to methane ratio (C_2/C_1) versus the $\delta^{13}\text{C}$ value of methane (C_1), as normalized by the same ratio in the standard Vienna PeeDee Belemnite (VPDB), for gas collected from fumaroles, frying pans, and pools at Yellowstone. Fields for thermogenic and biogenic after Pohlman and others (2009). Numbers listed in the legend correspond to the sample groups as defined in table 1.

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2003: Lizette Christiansen, Cathy Goff, Fraser Goff, Shaul Hurwitz, Gari Mayberry, Lisa Morgan, Andy Ouimette, Pat Shanks

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2006: Hank Heasler, Shaul Hurwitz, Cheryl Jaworowski, John King, Cindy Werner

2007: Atosa Abedini, Stefano Caliro, Carlo Cardellini, Giovanni Chiodini, Italo Giarretta, Luca Guglielmetti, Franco Tassi, Dario Tedesco, Cindy Werner

2008: Angie Diefenbach, Shaul Hurwitz, Alison Philips

2009: Sheryl Akagi, Bob Yokelson

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