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Journal of volcanology and geothermal research

Journal of Volcanology and Geothermal Research 162 (2007) 149-171

www.elsevier.com/locate/jvolgeores

Spatial and temporal geochemical trends in the hydrothermal system of Yellowstone National Park: Inferences from river solute fluxes

Shaul Hurwitz^{a,*}, Jacob B. Lowenstern^{a,1}, Henry Heasler^{b,2}

^a U.S. Geological Survey, Menlo Park, CA, USA ^b Yellowstone National Park, Mammoth, WY, USA

Received 29 June 2006; received in revised form 18 January 2007; accepted 25 January 2007 Available online 21 February 2007

Abstract

We present and analyze a chemical dataset that includes the concentrations and fluxes of HCO_3^- , SO_4^+ , CI^- , and F^- in the major rivers draining Yellowstone National Park (YNP) for the 2002–2004 water years (1 October 2001 – 30 September 2004). The total (molar) flux in all rivers decreases in the following order, $HCO_3^->Cl^->SO_4^{2-}>F^-$, but each river is characterized by a distinct chemical composition, implying large-scale spatial heterogeneity in the inputs of the various solutes. The data also display nonuniform temporal trends; whereas solute concentrations and fluxes are nearly constant during base-flow conditions, concentrations decrease, solute fluxes increase, and HCO_3^-/CI^- , and $SO_4^2^-/CI^-$ increase during the late-spring high-flow period. $HCO_3^-/SO_4^2^$ decreases with increasing discharge in the Madison and Falls Rivers, but increases with discharge in the Yellowstone and Snake Rivers. The non-linear relations between solute concentrations and river discharge and the change in anion ratios associated with spring runoff are explained by mixing between two components: (1) a component that is discharged during base-flow conditions and (2) a component associated with snow-melt runoff characterized by higher HCO_3^-/Cl^- and SO_4^{2-}/Cl^- . The fraction of the second component is greater in the Yellowstone and Snake Rivers, which host lakes in their drainage basins and where a large fraction of the solute flux follows that of ice cover in the spring months. Although the total river HCO_3^- flux is larger than the flux of other solutes (HCO₃/Cl⁻ \approx 3), the CO₂ equivalent flux is only ~1% of the estimated emission of magmatic CO₂ soil emissions from Yellowstone. No anomalous solute flux in response to perturbations in the hydrothermal system was observed, possibly because gage locations are too distant from areas of disturbance, or because of the relatively low sampling frequency. In order to detect changes in river hydrothermal solute fluxes, sampling at higher frequencies with better spatial coverage would be required. Our analysis also suggests that it might be more feasible to detect large-scale heating or cooling of the hydrothermal system by tracking changes in gas and steam flux than by tracking changes in river solute flux. Published by Elsevier B.V.

Keywords: Yellowstone; hydrothermal; river discharge; river chemistry; chloride flux; heat flux; temporal trend

* Corresponding author. Tel.: +1 650 329 4441. E-mail addresses: shaulh@usgs.gov (S. Hurwitz).

jlwnstrn@usgs.gov (J.B. Lowenstern), Henry_Heasler@nps.gov (H. Heasler).

0377-0273/\$ - see front matter. Published by Elsevier B.V. doi:10.1016/j.jvolgeores.2007.01.003

1. Introduction

The Yellowstone Plateau volcanic field hosts Earth's largest "restless" caldera (Newhall and Dzurisin, 1988; Christiansen, 2001) and is characterized by abundant seismicity (Waite and Smith, 2002), cycles of uplift and subsidence (e.g., Dzurisin et al., 1990, 1994; Wicks

¹ Tel.: +1 650 329 5238.

² Tel.: +1 307 344 2441.

et al., 1998, 2006), and an active hydrothermal system. Hydrothermal features include geysers, fumaroles, mud pots, thermal springs (e.g., Fournier, 1989), and hydrothermal explosion craters (Muffler et al., 1971). Many workers have characterized the chemistry of these hydrothermal features (e.g. Gooch and Whitfield, 1888; Allen and Day, 1935; Rowe et al., 1973; Thompson and DeMonge, 1996; Xu et al., 1998; Kharaka et al., 2002), including gas composition and flux (e.g. Gunter and Musgrave, 1966; Kennedy et al., 1987; Goff and Janik, 2002; Werner and Brantley, 2003). Such studies reveal large spatial variability in the chemical characteristics of thermal features and some temporal variability (Fournier, 1989; Fournier et al., 2002).

It is important to understand whether hydrothermal fluid compositions or fluxes correlate with other signs of unrest in the caldera such as seismicity and deformation (Lowenstern et al., 2006). Because of the tremendous number and diversity of thermal features, it remains daunting to identify individual features that might serve as proxies for the hydrothermal system. Rivers provide some advantages over sampling individual thermal features, because they integrate chemical fluxes over a very large area and therefore, river fluxes may reveal large-scale spatial patterns. Also, frequent and continuous sampling of the rivers is technically possible, whereas it is very difficult to sample and measure the discharge of myriad thermal features at Yellowstone on a continuous basis.

Intermittent sampling of the large rivers draining Yellowstone National Park (YNP) (Fig. 1) began in the 1960s (Fournier et al., 1976) and continuous sampling has been carried out for more than 20 years. Chloride fluxes were calculated to assess possible changes in heat output (Norton and Friedman, 1985; Friedman and Norton, in press), and possible correlations with vertical displacements of the caldera floor and large earthquakes (Fournier, 1989; Dzurisin et al., 1990, 1994). To date, no such correlations have been observed (Ingebritsen et al., 2001; Fournier, 2004). Inter-annual changes in Cl⁻ flux do display a positive correlation with river discharge (Fig. 2), suggesting that precipitation and river discharge are the major controls on Cl⁻ flux.

In this paper, we present and evaluate a chemical dataset that includes the concentrations and fluxes of HCO_3^- , SO_4^{2-} , CI^- , and F^- in rivers draining YNP for the 2002–2004 water years (1 October 2001 – 30 September 2004). These solutes were chosen because they are likely derived in part, from the magmatic volatiles CO₂, SO₂, H₂S, HCl, HF (Symonds et al., 2001). Weekly to monthly sampling enables the

examination of spatial and temporal patterns of flux among the different solutes, which in turn, permits inference of large-scale processes in the hydrothermal system, as well as the influence of climatic and hydrologic factors.

2. The geochemistry of the YNP hydrothermal system

A prominent geochemical model of the YNP hydrothermal system (Truesdell and Fournier, 1976; Fournier, 1989) invokes a single "parent" fluid rich in dissolved CO₂ and H₂S and containing ~400 ppm Cl⁻ with little SO₄²⁻ and HCO₃⁻. The estimated depth of this parent reservoir is between 2 and 5 km at a temperature of about 340 to 370 °C (Fournier, 1989). This "parent" water is modified upon flow to the surface (and in some cases at the surface) by boiling, gas-water-rock interaction, mixing, and dilution to form chemically diverse surficial hydrothermal waters.

This model is supported by the oxygen and deuterium isotopic composition of the thermal waters, which indicate boiling of deeply circulated waters that interacted with rock at high temperatures. The waters appear to have originated predominantly as winter precipitation in the Gallatin and northern Absaroka Ranges (Fig. 1), north and northwest of the caldera (Truesdell et al., 1977; Rye and Truesdell, 1993; Kharaka et al., 2002). Any possible magmatic–water contribution to the hydrothermal system is less than a few percent (Truesdell et al., 1977).

Thermal springs characterized by neutral to slightly alkaline water, relatively high concentrations of chloride and SiO₂, and siliceous sinter deposition (and some travertine deposition) are mainly found in geyser basins along the Firehole and Gibbon Rivers and in Shoshone and Heart Lake Geyser Basins in the Snake River drainage (Fig. 1). Variations in chloride and bicarbonate concentrations in thermal waters from these basins result from varying degrees of conductive cooling and decompressional boiling and from mixing of different thermal waters (Fournier, 1989). In waters that do not boil, CO₂ remains in solution forming carbonic acid (H₂CO₃) which, as temperatures decline, reacts with the wall rock, resulting in higher bicarbonate concentrations (Fournier, 1989). In Norris Geyser Basin, where the estimated temperatures for the shallow reservoirs are possibly higher than 300 °C (Fournier et al., 2002), waters have undergone considerable boiling and therefore have low bicarbonate concentrations.



Fig. 1. Map of the Yellowstone National Park region showing the major rivers and the gaging and sampling sites mentioned in this study: YR – Yellowstone River, GR – Gardner River, BR – Boiling River, GIBR – Gibbon River, FHR – Firehole River, MR – Madison River, YFB – Yellowstone River at Fishing Bridge near Yellowstone Lake outlet, SR – Snake River, FR – Falls River, HFR – Henrys Fork River. Also shown are the locations of some major geyser basins and other thermal areas: NMC – Norris–Mammoth Corridor, NGB – Norris Geyser Basin, CH – Crater Hill, MV – Mud Volcano, WTB – West Thumb Basin, UGB – Upper Geyser Basin, MGB – Midway Geyser Basin, LGB – Lower Geyser Basin, SGB – Shoshone Geyser Basin, HLGB – Heart Lake Geyser Basin, and RM – Roaring Mountain. The Yellowstone National Park boundary is shown in dash-dot lines, and state borders are shown in dashed lines. Also shown are the Yellowstone Caldera (grey area) and its two resurgent domes: MLD – Mallard Lake Dome and SCD – Sour Creek Dome.

The steam from boiling alkaline–chloride waters contains H_2S , which oxidizes to H_2SO_4 when it comes into contact with air (±thermophilic life-forms) in perched groundwater. The resulting acidic water alters the volcanic rock to clays and other alteration minerals, forming "acid sulfate" terrain (White et al., 1971). Acid sulfate regions are characterized by fumaroles and mud pots with limited liquid–water discharge, low chloride, and high sulfate concentrations. At YNP the acid sulfate areas are prevalent in topographically elevated areas in the eastern part of the Yellowstone Caldera, along the Norris–Mammoth Corridor, and in a few elevated areas along the Firehole River drainage (Fig. 1). Some of the acid sulfate springs and seeps in the eastern part of the caldera also contain high concentrations of hydrocarbons, probably originating from shallow sediments and sedimentary rocks (Love and Good, 1970; Clifton et al., 1990; Goff and Janik, 2002).

Other HCO_3^- -rich thermal waters are found at Mammoth Hot Springs (Fig. 1). These waters flow through a thick sequence of sedimentary rocks that includes limestone, dolomite, and gypsum-bearing shales (Pierce et al., 1991) and consequently, are rich



Fig. 2. Annual river discharge (solid lines and filled symbols) and chloride flux (dashed lines and empty symbols) normalized to the annual average for water years 1990–2004. The chloride flux for water years 1990 to 2001 is from Friedman and Norton (in press) and for 2002–2004 from this study. No CI^{-} flux data is available for water years 1995 and 1996. The horizontal dashed line represents the 1990–2004 annual average river discharge and CI^{-} flux. The shaded area represents data reported in this study.

in bicarbonate, sulfate and chloride and precipitate travertine.

3. Hydrology

The four major rivers that drain most of YNP are the Madison, Yellowstone, Snake, and Falls Rivers (Fig. 1). Henrys Fork of the Snake River drains a few small tributaries along the western park boundary and accounts for $\sim 7\%$ of the total chloride discharge from YNP (Friedman and Norton, in press). Available data from Henrys Fork is presented in Table 1, but was excluded from our analysis because the gage on the river is located downstream from the large manmade Island Park Reservoir and the temporal solute flux trends are controlled by the reservoir (Fig. 1).

The Yellowstone River (Fig. 1) has the largest drainage area within the park (Table 1). In addition to being the outlet from Yellowstone Lake, it captures the discharge of a group of acid sulfate springs in the Mud Volcano area, as well as springs along the Grand Canyon of the Yellowstone River, the Lamar River, and the Gardner River, which itself captures the discharge of many springs along the Norris–Mammoth Corridor (Fig. 1). The majority of the flow (~90%) from the travertine-depositing springs at Mammoth Hot Springs

is captured by the gage on the Boiling River ("Hot River") (Sorey et al., 1991), located ~200 m upstream from the Gardner River gage (Fig. 1). Between 1988 and 1990 the percentage of Cl⁻ issuing from Mammoth Hot Springs, and flowing through Boiling River was 90–95% of the total Cl⁻ flux through the Gardner River during base-flow and 60–80% during periods of high river discharge (Sorey et al., 1991). Thus, Cl⁻ flux from the Gardner River is dominated by discharge from Mammoth Hot Springs, and has only a small component derived from the acid sulfate springs along the Norris–Mammoth Corridor.

The Madison River includes the flow from the Firehole River, which drains the Upper, Midway and Lower Geyser Basins, and the Gibbon River, which drains the Norris and Gibbon Geyser Basins (Fig. 1). To the south, the Snake River drains the Shoshone and Heart Lake Geyser Basins, Lewis Lake and the travertine-depositing Snake River Hot Springs. The Falls River drains the thermal features of the Bechler Canyon and Boundary Creek, as well as the Pitchstone Plateau in the southwest corner of YNP.

The total annual water discharge through the four major rivers in water years 2002–2004 was lower than the annual average for water years 1990–2004 (Fig. 2). Discharge in the 2001 water year was the lowest

Table 1 Water discharge ($\times 10^8$ m³) and solute flux (kt/yr) from the Yellowstone NP rivers for water years 2002–2004

	Yellowstone River ^a	Madison River ^a	Snake River ^a	Falls River ^a	Total ^b	Gardner River ^c	Boiling River ^d	Gibbon River ^e	Firehole River ^e	Henrys Fork
USGS Station ^f	6191500	6037500	13010065	13046995		6191000	6190540	6037100	6036905	13046000
Drainage area (km ²)	6783	1088	1259	850	9980	523	N/A	126	730	2694
WY 2002										
No. samples	23	28	24	20		27	0	0	0	26
Discharge	$24.4(58)^2$	3.8 (9)	7.3 (17)	6.6 (16)	42.1	1.6 (7)	N/A	N/A	N/A	11.3
Cl ⁻ flux ^d	15 (31)	23 (46)	6 (12)	5 (11)	50 (1.4)	4 (24)	N/A	N/A	N/A	3
SO_4^{2-} flux	41 (68)	6 (10)	11 (19)	2 (3)	60 (0.6)	14 (34)	N/A	N/A	N/A	4
HCO ₃ ⁻ flux	138 (50)	51 (19)	45 (17)	39 (14)	273 (4.5)	22 (16)	N/A	N/A	N/A	80
F ⁻ flux	1.2 (20)	2.6 (42)	0.9 (14)	1.4 (23)	6.2 (0.3)	0.2 (13)	N/A	N/A	N/A	2
WY 2003										
No. samples	29	31	25	23		30	24	20	18	0
Discharge	24.8 (59)	3.9 (9)	6.7 (16)	7.0 (16)	42.4	1.6 (6)	0.2 (12)	1.1 (30)	2.4 (63)	11.4
Cl ⁻ flux ^d	16 (30)	24 (47)	6 (11)	6 (11)	51 (1.4)	3 (21)	3 (93)	6 (23)	17 (70)	N/A
SO_4^{2-} flux	47 (72)	6 (9)	11 (16)	2 (3)	65 (0.7)	12 (26)	11 (88)	3 (45)	3 (54)	N/A
HCO ₃ ⁻ flux	126 (49)	51 (20)	42 (16)	40 (15)	259 (4.2)	18 (14)	3 (19)	11 (22)	33 (64)	N/A
F ⁻ flux	1.3 (21)	2.6 (42)	0.8 (13)	1.5 (24)	6.3 (0.3)	0.2 (12)	< 0.1 (33)	0.4 (16)	2.1 (79)	N/A
WY 2004										
No. samples	32	27	26	11		35	22	19	21	13
Discharge	20.9 (54)	3.7 (10)	6.7 (17)	7.1 (19)	38.4	1.5 (7)	0.2 (13)	1.0 (26)	2.5 (68)	11.9
Cl ⁻ flux ^d	15 (30)	23 (46)	6 (12)	6 (12)	49 (1.4)	3 (24)	3 (80)	5 (24)	17 (75)	N/A
SO_4^{2-} flux	39 (68)	6 (10)	10 (18)	2 (3)	57 (0.6)	13 (33)	10 (76)	3 (44)	3 (56)	N/A
HCO ₃ ⁻ flux	124 (49)	51 (20)	40 (16)	40 16)	254 (4.2)	21 (17)	4 (18)	10 (20)	32 (64)	N/A
F^- flux	1.2 (19)	2.6 (41)	0.8 (13)	1.7 (26)	6.3 (0.3)	0.2 (14)	< 0.1 (29)	0.4 (15)	2.1 (81)	N/A

^a Numbers in parentheses in this column is the percentage of the total solute flux from the park.

^b Numbers in parentheses in this column are molar fluxes (10⁶ mol/yr).

^c Numbers in parentheses are the percentage of the flux through the Yellowstone River.

^d Numbers in parentheses are the percentage of the flux through the Gardner River.

^e Numbers in parentheses in the values for the Gibbon River and Firehole River are the percentage of the flux through the Madison River.

^f Discharge data and other parameters for the rivers in the table can be downloaded from http://volcanoes.usgs.gov/yvo/hydro_data.html.

since 1990. The hydrographs show the YNP rivers are snowmelt-dominated, with base-flow from late September–October through April followed by rapid increase in discharge following snowmelt. After peaking in late May–June, the discharge decreases rapidly (<2 months) to base-flow conditions, except for the Yellowstone River where discharge decreases gradually to base-flow conditions over 2–3 months (Figs. 3a–9a).

4. Sampling and analytical methods

Following the protocols of Friedman and Norton (in press), water samples were collected from the four major rivers and the Gardner River between October 2001 and September 2004. Starting in water year 2003, samples were also collected from the Firehole, Gibbon, and Boiling Rivers (Fig. 1). The strategy was to sample once per month between October and March, twice a month in April and September, and once a week between May and August, for a total of 28 samples per year for each river. However, the actual number of collected samples

was less in most cases; in particular, numerous Falls River samples are missing (Table 1).

Concentrations of Cl⁻, F⁻, and SO₄²⁻ were determined with a Dionex ion chromatograph DX-300 at the U.S. Geological Survey in Menlo Park, California. Analytical errors for these constituents are typically <2%. Total alkalinity as HCO_3^- was determined on stored samples, usually several months after collection. Ten milliliters of sample were titrated with 0.05 N H₂SO₄ to the bicarbonate end-point. The analytical error in alkalinity concentrations is roughly ±5%.

Stream discharge at the time of sampling was obtained from the U.S. Geological Survey's stream gaging data (http://volcanoes.usgs.gov/yvo/hydro_data.html). The automated stream discharge measurements are made every 15 min, and the discharge at each of the rivers was measured manually several times each year to establish rating curves. At low discharges, differences between the manual and automatic measurements are typically less than 5%. At high flow rates, errors can be higher.



Fig. 3. (a) Water discharge (thick solid line) and the fraction of the discharge from the Gardner River and the discharge of the Yellowstone River at the Yellowstone Lake outlet (thin solid lines); (b) CI^- concentration (empty circles) and flux (filled circles); (c) HCO_3^- concentration (empty circles) and flux (filled circles); (d) SO_4^{2-} concentration (empty circles) and flux (filled circles); (e) molar HCO_3^-/CI^- ; and (f) molar SO_4^{2-}/CI^- in the Yellowstone River during 2002–2004 water years. The shaded areas mark the periods of increased discharge in May and June, and the numbers to their right are the percentage of the annual flux during these two months.

4.1. Flux calculations

The annual flux of solutes was calculated following the protocols of Friedman and Norton (in press). The instantaneous chloride fluxes were calculated by multiplying the solute concentrations of the samples by the river discharges recorded at the time of sample collection. Annual summations were made by integrating between calculated values for each sample from the beginning of the water year (October 1) to the end of the



Fig. 4. (a) Water discharge (dashed line) and the fraction of the Firehole and Gibbon Rivers discharge (solid lines); (b) CI^- concentration (empty circles) and flux (filled circles); (c) HCO_3^- concentration (empty circles) and flux (filled circles); (d) SO_4^{2-} concentration (empty circles) and flux (filled circles); (e) molar HCO_3^-/CI^- , and (f) molar SO_4^{2-}/CI^- in the Madison River during 2002–2004 water years.

water year (September 30). If samples were not collected on October 1, September 30, or within a scheduled time frame, we calculated the expected instantaneous flux by multiplying the average daily for that date by the chloride concentration determined by a

fit to the chloride–discharge relation for the rest of the year (Friedman and Norton, in press).

There are several factors that contribute to uncertainties in the determination of the total annual flux: (1) error in the measurements of stream discharge, usually less than 5% during base-flow, but significantly greater during the spring runoff; (2) analytical error of less than 2% in the measurement of Cl⁻, SO_4^{2-} , and F⁻ concentrations and up to 5% in the determination of HCO₃⁻; (3) discharge through groundwater and small tributaries crossing YNP boundaries; and (4) the error associated with the integration of solute flux measurements between two consecutive measurements.

The contribution of precipitation-derived solutes to the total solute flux is small and was calculated to be



Fig. 5. (a) Water discharge; (b) CI^{-} concentration (empty circles) and flux (filled circles); (c) HCO_{3}^{-} concentration (empty circles) and flux (filled circles); (d) SO_{4}^{2-} concentration (empty circles) and flux (filled circles); (e) molar HCO_{3}^{-}/CI^{-} ; and (f) molar SO_{4}^{2-}/CI^{-} in the Snake River during 2002–2004 water years. The shaded areas mark the periods of increased discharge in May and June, and the numbers to their right are the percentage of the annual flux during these two months.



Fig. 6. (a) Water discharge; (b) Cl^- concentration (empty circles) and flux (filled circles); (c) HCO_3^- concentration (empty circles) and flux (filled circles); (e) molar HCO_3^-/Cl^- ; and (f) molar SO_4^{2-}/Cl^- in the Falls River during 2002–2004 water years.

approximately 4% for Cl^- and 14% for SO_4^{2-} . This calculation assumes conservative (high) concentrations of Cl^- (0.5 mg/l) and SO_4^{2-} (2 mg/l) in precipitation

(Kharaka et al., 2002). We estimate HCO_3^- concentrations in precipitation to be <10 mg/l, implying a maximum contribution of 15% to the calculated river HCO_3^- flux.

5. Data

5.1. Spatial and temporal trends of solute discharge

The chemical data display large spatial variability; waters from each river are characterized by distinctive

anion concentrations (Table 2 and Figs. 3b-d-9b-d), fluxes (Table 1 and Figs. 3b-d-9b-d, 12), anion ratios (Table 3; Figs. 3e-f-9e-f), and chemical compositions (Figs. 10 and 11). Solute concentrations reported in this study are all in mg/l and anion ratios are molar. The complete dataset, which includes anion concentrations



Fig. 7. (a) Water discharge; (b) $C\Gamma$ concentration (empty circles) and flux (filled circles); (c) HCO_3^- concentration (empty circles) and flux (filled circles); (d) SO_4^{2-} concentration (empty circles) and flux (filled circles); (e) molar $HCO_3^-/C\Gamma^-$; and (f) molar $SO_4^{2-}/C\Gamma^-$ in the Gardner River during 2002–2004 water years.





Fig. 8. (a) Water discharge with inset highlighting the increased discharge following the November 3, 2002 Denali earthquake (vertical dashed line); (b) $C\Gamma$ concentration (empty circles) and flux (filled circles); (c) HCO_3^- concentration (empty circles) and flux (filled circles); (d) SO_4^{2-} concentration (empty circles) and flux (filled circles); and (e) $HCO_3^-/C\Gamma$; and (f) molar $SO_4^{2-}/C\Gamma$ in the Firehole River during 2003–2004 water years.

in all samples, the corresponding water discharge, and the calculated instantaneous solute fluxes, can be found at http://volcanoes.usgs.gov/yvo/hydrofluxdata.html.

the various rivers differs drastically for each of the measured solutes (Table 1 and Fig. 12).

The total (molar) flux from the four major rivers decreases in the following order $HCO_3^->Cl^->SO_4^{2-}>F^-$ (Table 1). However, the distribution of solute flux from

5.1.1. Yellowstone River drainage

The solute flux (Fig. 3b–d) and anion composition (Figs. 10 and 11) of Yellowstone River waters at Corwin



Fig. 9. (a) Water discharge; (b) CI^- concentration (empty circles) and flux (filled circles); (c) HCO_3^- concentration (empty circles) and flux (filled circles); (d) SO_4^{2-} concentration (empty circles) and flux (filled circles); (e) HCO_3^-/CI^- ; and (f) molar SO_4^{2-}/CI^- in the Gibbon River during 2003–2004 water years. The three dashed vertical lines represent the eruptions of Steamboat Geyser, and the shaded area represents the large thermal disturbance in Norris Geyser Basin in the summer of 2003.

Springs (Fig. 1) reflect input from Yellowstone Lake, Lamar River, and Gardner River (which receives input from the Boiling River) (Fig. 1). Yellowstone River anion compositions trend from a HCO₃⁻-rich endmember during spring runoff to more Cl⁻- and SO₄²⁻enriched compositions like the Boiling River (draining Mammoth Hot Springs) during base-flow conditions (Fig. 10). Similarly, Gardner River waters represent mixing between a Boiling River end-member and a HCO_3^- -rich end-member, but have larger variability. The Yellowstone, Gardner and Boiling Rivers are also characterized by relatively low F^-/Cl^- (Fig. 11).

Table 2 Range of solute concentrations (in mg/l) in Yellowstone NP rivers for water years 2002–2004

	Cl	F^{-}	SO_4^{2-}	HCO_3^-
Yellowstone River				
WY 2002	2-19	0.2 - 1.2	6-51	38-102
WY 2003	1 - 17	0.2 - 1.2	4-46	27-92
WY 2004	2 - 18	0.2 - 1.1	6-48	36-98
Madison River				
WY 2002	30-78	3.8-8.2	10 - 20	74-156
WY 2003	22-73	2.8 - 8.0	7-18	53-155
WY 2004	29-76	3.6-8.2	8-18	92-156
Snake River				
WY 2002	3-23	0.6 - 2.7	6-35	43-101
WY 2003	2 - 20	0.6 - 2.5	6-31	47-100
WY 2004	4-22	0.6 - 2.7	7-37	43-105
Falls River				
WY 2002	3-16	1.0 - 3.8	2-4	31-100
WY 2003	3-15	0.9-3.6	1-4	26-89
WY 2004 ^a	3-11	1.3-3.3	1-3	28-61
Firehole River				
WY 2003	33-81	4.3-9.7	7-15	65-149
WY 2004	46-83	5.9-9.7	9-16	90-153
Gibbon River				
WY 2003	17-77	1.6-4.6	12-35	40-132
WY 2004	30-75	2.6 - 4.6	18-35	64-132
Gardner River				
WY 2002	6-61	0.5 - 1.6	24-220	86-258
WY 2003	4-46	0.5 - 1.7	16-163	36-182
WY 2004	7-51	0.5 - 1.6	26-184	88-205
Boiling River				
WY 2003	102-146	1.8 - 2.4	375-525	110-211
WY 2004	112-153	2.0 - 2.6	406-550	122-230

⁴ Many samples from water year 2004 are missing.

The Yellowstone River accounts for 54–59% of the total water discharge from YNP, but its percentage of the YNP SO_4^{2-} flux (68–72%) is greater, and the percentages of HCO_3^- (49–50%), Cl⁻ (30–31%) and F⁻ (19–21%) fluxes are lower (Table 2; Fig. 12). The temporal trends of solute flux (Fig. 3b–d) and anion ratios (Fig. 3e–f) are dominated by a large (\leq 30-fold) discharge variation associated with spring runoff (Fig. 3a). For example, runoff during May and June accounts for 35–44% of the HCO_3^- (Fig. 3c) and 23–35% of the SO_4^{2-} (Fig. 3d) flux for the Yellowstone River, annually.

The rapid increase in Yellowstone River discharge during the spring coincides with thaw of the ice cap over Yellowstone Lake. In the winter, when the lake is frozen, the discharge at Fishing Bridge near the lake outlet (Fig. 1) accounts for 10-25% of the discharge at the Corwin Springs gage, but following the ice-thaw, discharge increases by as much as 75% (Fig. 3a). Prior to, and concurrent with the large outflow from Yellowstone Lake, river discharge increases (Fig. 3a), con-

centrations of solutes decrease (Figs. 3b–d and 13a), fluxes increase (Fig. 3b–d), and HCO_3^-/Cl^- , SO_4^{2-}/Cl^- (Fig. 3e–f), and HCO_3^-/SO_4^{2-} increase (Fig. 14a).

The proportional contribution of water and solutes from the Gardner River to the Yellowstone River increases during base-flow conditions (Figs. 3a and 15). Boiling River contributes 80-93% of the Cl⁻ load and 76-88% of the SO₄²⁻ load in the Gardner River (Table 1), requiring overall small contributions of these anions from the entire Norris–Mammoth Corridor (Fig. 1). Boiling River contributions of HCO₃⁻ and F⁻ are low (Table 1). Discharge in the Boiling River varies by less than a factor of two, and consequently, there are no observable annual patterns in fluxes.

5.1.2. Madison River drainage

There are no known thermal features downstream from the Firehole River–Gibbon River confluence (Fig. 1). Therefore, solute flux (Fig. 4b–d) and the chemical composition (Figs. 10 and 11) of the Madison River at the gage near West Yellowstone almost entirely reflect inputs from the Firehole and Gibbon Rivers. The fluxes from the Firehole and Gibbon River accounted for

Table 3

Molar anion ratios of solutes from YNP Rivers derived from the annual flux

	SO4 ²⁻ /Cl ⁻	HCO ₃ /Cl ⁻	HCO_3^-/SO_4^{2-}
WY 2002			
Yellowstone	1.0	5.2	5.3
Madison	0.1	1.3	13.3
Snake	0.7	4.2	6.3
Falls	0.1	4.2	32.8
TOTAL	0.4	3.2	7.1
Gardner	1.4	3.5	2.5
WY 2003			
Yellowstone	1.1	4.7	4.3
Madison	0.1	1.2	13.6
Snake	0.7	4.2	6.3
Falls	0.1	4.1	35.8
TOTAL	0.5	2.9	6.3
Gardner	1.4	3.1	2.2
Boiling	1.3	0.7	0.5
Firehole	0.1	1.1	16.2
Gibbon	0.2	1.2	6.6
WY 2004			
Yellowstone	1.0	4.9	5.0
Madison	0.1	1.3	14.0
Snake	0.6	3.9	6.0
Falls	0.1	4.0	34.8
TOTAL	0.4	3.0	7.1
Gardner	1.4	3.5	2.5
Boiling	1.3	0.8	0.6
Firehole	0.1	1.1	16.0
Gibbon	0.2	1.1	6.5



YNP river composition

Fig. 10. Ternary plot showing molar ratios of SO_4^{2-} -HCO₃-Cl⁻ in Yellowstone River during 2002–2004 water years. YR – Yellowstone River, GR – Gardner River, BR – Boiling River, GIBR – Gibbon River, FHR – Firehole River, MR – Madison River, SR – Snake River, FR – Falls River. The arrow indicates the change in compositions from periods of high water discharge to base-flow conditions in the Yellowstone and Snake Rivers.

89-94%, 93-99%, 100%, 84-86%, and 95-96% of the water, Cl⁻, SO₄²⁻, HCO₃⁻, and F⁻, respectively of the Madison River flux in water years 2003 and 2004

(Table 1). The Firehole River water discharge accounted for 61-68% of the Madison River discharge, but contributed a higher percentage of Cl⁻ (70-75%) and



Fig. 11. Molar ratio of fluoride to chloride as a function of chloride concentration in Yellowstone River during 2002-2004 water years.



Fig. 12. The distribution of the average annual flux during water years 2002-2004 of (a) water, (b) HCO₃⁻, (c) Cl⁻, (d) SO₄²⁻, and (e) F⁻ between the rivers of YNP. Abbreviations for rivers as in Fig. 1.

 F^{-} (79–81%), and a lower percentage of SO_4^{2-} (54–56%) (Table 1).

The composition of the Firehole River is characterized by approximately equal concentrations of Cl⁻ and HCO₃⁻, low SO₄²⁻ concentrations, and displays very little variability (Fig. 10). The Firehole River F⁻/Cl⁻, which is higher than the ratio in the Gibbon River, dominates the ratio in the Madison River (Fig. 11). Gibbon River waters are more enriched in SO₄²⁻ and display variability sub-parallel to the HCO₃⁻-Cl⁻ join. Water discharge from the Madison River accounts for only 9–10% of the total water discharge and SO_4^{2-} flux from YNP, but its contributions to Cl⁻ (46–47%), F⁻ (41–42%), and HCO₃⁻ fluxes (19–20%) are much greater (Table 2; Fig. 12). The increase in discharge from base-flow to spring runoff in the Madison River (three-fold variation or less; Fig. 4a), Firehole River (<2.5-fold; Fig. 8a), and Gibbon River (<5-fold; Fig. 9a) are relatively small and accordingly, the decrease in anion concentration (Fig. 13b) and the



Fig. 13. Concentrations of Cl^- (filled circles) and HCO_3^- (empty diamonds) as a function of river discharge in (a) Yellowstone River, (b) Madison River, (c) Snake River, and (d) Falls River.

temporal variability of solute fluxes (Figs. 4b–d, 8b–d, 9b–d) and anion ratios (Figs. 4e–f, 8e–f, 9e–f and 14b) is relatively small. Further, within the resolution of our analysis, the temporal flux variations in the Firehole River do not display any observable pattern (Fig. 8), and the Cl⁻ flux in the Madison River during water years 2002 and 2004 was nearly uniform (Fig. 4b). In contrast, the Gibbon River showed increased discharge, solute flux, HCO_3^-/Cl^- , and SO_4^{2-}/Cl^- ratios (Fig. 9) during spring runoff. A larger Gibbon River contribution to the Madison River was apparent during the summer of 2003, but not in water year 2004 (Figs. 4a and 16).

5.1.3. Snake River

Similar to the Yellowstone River, the composition of the Snake River varies from HCO_3^- -rich during spring runoff to a more $SO_4^{2^-}$ and Cl^- -enriched during base-flow (Fig. 10). F^-/Cl^- in the Snake River is variable with values larger than those in the Yellowstone River (Fig. 11). Higher F^-/Cl^- in both rivers occurs during spring runoff.

The Snake River accounts for 16-17% of the total water discharge and HCO₃⁻ flux and 16-19% of the SO₄²⁻ flux from YNP, but its contribution to the total Cl⁻ and F⁻ is slightly lower (Table 1; Fig. 12).



Fig. 14. Molar HCO_3^-/SO_4^{2-} as a function of river discharge in water years 2002–2004 in (a) Yellowstone River, (b) Madison River, (c) Snake River, and (d) Falls River.

Temporal solute flux trends (Fig. 5b–d) and anion ratios (Fig. 5e–f) in the Snake River are dominated by a large (i.e. ~30-fold) discharge variation associated with spring runoff (Fig. 5a), with a large concentration decrease (Figs. 5b–d and 13c), flux increase (Fig. 5b–d), and HCO_3^-/CI^- , SO_4^{2-}/CI^- (Fig. 5e–f), and HCO_3^-/SO_4^{2-} increase (Fig. 14c). For example, the fluxes of CI⁻, HCO_3^- and SO_4^{2-} in May and June accounted for 22–26%, 35–48%, and 23–32%, respectively of the annual fluxes in water years 2002–2004 (Fig. 5b–d).

Although there are no direct observations regarding the timing of ice-cap thaw on the three lakes in the Snake River drainage basin (Fig. 1), it probably coincides with the onset of increased river discharge, implying that a large fraction of the high HCO_3^- and F^- discharged during that period may be derived from the lakes.

5.1.4. Falls River

The dataset from the Falls River is missing many samples, mainly from water year 2004. The available data indicate that the composition is HCO_3^- -rich with low SO_4^{2-} and variable HCO_3^-/Cl^- . F^-/Cl^- in the Falls River are the largest and most variable of all the YNP rivers (Fig. 11).

The increase in discharge during the spring runoff (14 times the base-flow during water year 2002; Fig. 6a) is smaller than that in the Yellowstone and Snake Rivers, but



Fig. 15. Percentage of the Yellowstone River discharge and solute flux attributable to the Gardner River. The shaded areas represent the period of high river discharge in the late spring.



Fig. 16. Percentage of the Gibbon River water discharge and solute flux of the Madison River discharge and solute flux. The shaded areas represent the period of high river discharge in the late spring.

larger than in the Madison River. During spring runoff, solute concentrations decrease (Figs. 6b–d and 13d), fluxes increase (Fig. 6b–d) and HCO_3^-/Cl^- and SO_4^{2-}/Cl^- increase (Fig. 6e–f). In contrast to the pattern in the Yellowstone and Snake Rivers, but similar to the pattern in the Madison River, the HCO_3^-/SO_4^{2-} ratio decreased with increasing discharge (Fig. 14d).

The SO_4^{2-} contribution from the Falls River to the total YNP river load (3%) is smaller than the contribution of water (16–19%), Cl⁻ (11–12%) and HCO₃⁻ (14–16%), and significantly smaller than the contribution of F⁻, which accounts for approximately one-quarter of the total YNP load (Table 1; Fig. 12).

6. Relations between solute flux and perturbations in the hydrothermal system

Many researchers have observed changes in the behavior of thermal features at Yellowstone, resulting from earthquakes and ground deformation (Marler and White, 1975; Pitt and Hutchinson, 1982; Husen et al., 2004a; Wicks et al., 2006; Lowenstern et al., 2006). Nevertheless, hydrological monitoring of stream flow and chemistry has had limited success at identifying signals from geophysical phenomena. Several potential disturbances to the hydrothermal system occurred during the period of our study. During the period between October 2001 and September 2004 the three largest earthquakes in YNP had magnitudes of 3.1, 3.2, and 3.3 (http://www.seis.utah.edu/catalog/ynp.shtml). These three earthquakes, all of which occurred during periods of base-flow, did not result in noticeable changes in discharge or solute flux in any of the rivers. Another significant event followed the arrival of seismic waves from the M = 7.9 Denali fault (Alaska) earthquake on 3 November 2002 at 15:26 MST, 14 min after the main aftershock (Husen et al., 2004a). The seismic waves induced abundant triggered earthquakes throughout YNP, primarily close to major geyser basins and also caused changes to the eruption frequency of some geysers (Husen et al., 2004a,b). There appears to have been an increase in the Firehole River discharge between two consecutive measurements at 16:00 and 16:15 MST (Fig. 8a). However, a chemical sample obtained from the Firehole River 2 weeks later was normal (Fig. 8b-e).

In July 2003, a major thermal perturbation occurred at Norris Geyser Basin (Fig. 1), manifested by increased ground-surface temperatures and vegetation kill (Lowenstern et al., 2003). The Norris Geyser Basin anomaly was preceded by the formation of vigorous fumaroles west of Nymph Lake, just to the north of the basin, in March 2003. In addition, Steamboat Geyser (considered as the geyser with the highest eruption plume on Earth) erupted on March 26 and April 27, 2003, and then again on October 22. Previously, Steamboat Geyser erupted twice in 2002 and once in 2000 following a 9-year hiatus. However, no anomalous change in solute flux or anion ratios in response to these events was observed in data from the Gibbon River (Fig. 9), though the instantaneous fluxes of CI^- and SO_4^{2-} following the first Steamboat Geyser eruption were the largest during water years 2003 and 2004 (Fig. 9b, d). It appears that most of the hydrological and geochemical transients were observable only near the Norris Geyser Basin and not far downstream.

7. Discussion

7.1. Cause of temporal trends

The non-linear relationships between solute concentration and river discharge (Fig. 13), changes in anion ratios, and the increase in solute flux associated with spring runoff (Figs. 3-6) broadly represent mixing between two components: (1) a component that is discharged during most of the year (base-flow conditions) and (2) a component discharged during the runoff period that is characterized by high HCO_3^-/Cl^- and SO_4^{2-}/Cl^- . The contribution of the second component is greater in the Yellowstone and Snake Rivers, which host lakes in their drainage basins. The difference between the Yellowstone and Snake Rivers on the one hand, and the Madison and Falls Rivers on the other, is also manifested by the different HCO_3^{-}/SO_4^{2-} discharge relationships (Fig. 14). This ratio decreases with increasing discharge in the Madison and Falls Rivers, but increases with discharge in the Yellowstone and Snake Rivers, suggesting that the composition of the dilute component associated with spring runoff differs throughout the park.

Previous studies proposed that the increase in $Cl^$ flux during spring runoff is caused by entrapment of chloride in frozen ground during the winter months followed by subsequent release of the chloride during the spring thaw (Fournier et al., 1976). Friedman and Norton (1990, in press) rejected this hypothesis, arguing that snow cover insulates the ground and prevents the soil from freezing and that thermal areas remain unfrozen and free of snow in the winter. As an alternative it was proposed that chloride flux increase during the runoff period is caused by increased groundwater head in shallow aquifers and a larger hydraulic gradient towards the rivers (Friedman and Norton, 1990, in press; Ingebritsen et al., 2001). A potential cause for the smaller relative increase in Cl^- flux in the Madison River, as compared with the Snake and Yellowstone Rivers, is less snow accumulation, and less snowmelt recharge in the Madison River drainage (Friedman and Norton, 1990, in press).

In addition to the increased flux induced by larger hydraulic gradients towards the rivers during spring runoff (Ingebritsen et al., 2001; Friedman and Norton, in press), the data presented in this study supports earlier studies (Fournier et al., 1976; Ingebritsen et al., 2001) where it was suggested that a large fraction of the enhanced solute flux in the Yellowstone and Snake Rivers is due to winter storage in lakes. During the winter months the lakes freeze and outflow is restricted. However, during this period, hydrothermal flux into the lake is characterized by high HCO₃/Cl⁻ and HCO₃/SO₄²⁻ (Balistrieri et al., in press; Gemery et al., in press), which affects the chemistry of lake waters (Theriot et al., 1997; Gemery et al., in press). When the ice cap melts, 70-80% of the total discharge measured on the Yellowstone River in Corwin Springs comes from Yellowstone Lake (Fig. 6a). The large outflow from the lakes carries the excess solutes that accumulated during the winter as evident from the elevated HCO_3^-/Cl^- (Figs. 3e and 5e), SO_4^{2-}/Cl^- (Figs. 3f and 5f), and HCO_3^-/SO_4^{2-} (Fig. 14a, c).

7.2. The dominance of CO_2

The total river fluxes and the HCO_3^-/Cl^- ratios indicate that the dominant anion in the rivers is HCO_3^- (Tables 1 and 3). This suggests that tracking $HCO_3^$ changes in rivers might reveal changes in the hydrothermal system in response to intrusive activity. However, since the river CO_2 -equivalent flux (as HCO_3^-) from YNP is only 1–2% of the 45±16 kt/day of diffuse CO_2 flux (Werner and Brantley, 2003), it is unclear how small changes in pressure and temperature in the subsurface could affect partitioning of CO_2 between liquid and vapor phases in the hydrothermal reservoir. Such partitioning could complicate any direct correlation between magmatic degassing and $HCO_3^$ flux through the rivers.

7.3. $C\Gamma$ flux, $C\Gamma$ sources, deformation and calculated heat flux

The advective heat output from YNP as calculated by the Cl⁻ inventory method (Ellis and Wilson, 1955; Fournier, 1979) and represented by the Cl⁻ flux from rivers is 6.5 GW (Friedman and Norton, in press). This calculated heat output is based on the premise that all the thermal features in YNP are derived from a single parent fluid with ~400 mg/l Cl⁻ and an enthalpy of 1600 kJ/kg (~340 °C; Truesdell and Fournier, 1976; Fournier, 1989). Based on 19 years of measurements, Friedman and Norton (in press) concluded that the "thermal" (e.g. non-meteoric) component of the Cl⁻ flux from YNP rivers declined by 10% between 1982 and 2001. The statistical analysis of Ingebritsen et al. (2001), which was based on the same dataset, implied that in the Firehole, Gibbon and Madison Rivers there is a declining trend in the flux of "thermal chloride", but the Yellowstone, Snake, and Falls Rivers show no statistically significant trends. Friedman and Norton (in press) suggest that "decreased output of thermal water from the Yellowstone system may be a result of volcanotectonic changes related to subsidence of the Yellowstone Caldera".

Whether or not a single parent fluid resides at the base of all Yellowstone hydrothermal areas, it is clear that Cl⁻ and other anions are not discharged in a homogeneous manner. To demonstrate this variability, we calculated the flux of each anion per unit area in each of the drainage basins (Table 4). The large range of calculated values illustrates the highly non-uniform flux distribution. Under the assumption of a single, uniform parent fluid, such data imply large-scale (tens of kilometers) lateral redistribution of Cl⁻ in the subsurface. Perhaps magmatic volatiles rise beneath the elevated eastern parts of the caldera, where magma is shallow (Miller and Smith, 1999) and much of the current crustal deformation occurs (e.g. Wicks et al., 1998, 2006). The soluble magmatic gases (HCl, HF, HBr) are then dissolved in groundwater and transported laterally towards the relatively low-elevation areas where Cl-rich fluids discharge (e.g., the Firehole River geyser basins), whereas the less soluble gases (CO₂ and H₂S) are exsolved from the thermal waters, and discharged in the high-elevation, "acid sulfate" areas. The lateral migration of Cl⁻-rich, hydrothermal fluids may take decades or longer; therefore, even significant changes in river Cl⁻ flux may not relate to concurrent events of magmatic unrest. Ingebritsen and Sorey (1988) list several

Table 4

Mean annual solute flux per area (equivalent/m²/yr) in YNP drainage basins for water years 2002-2004

	Cl ⁻	SO_4^{2-}	HCO_3^-	F^{-}
Yellowstone River	0.06	0.03	0.31	0.01
Madison River	0.60	0.03	0.77	0.13
Snake River	0.13	0.04	0.55	0.04
Falls River	0.19	0.01	0.76	0.10
Gardner River	0.19	0.13	0.63	0.02
Firehole River	0.65	0.02	0.73	0.15
Gibbon River	1.21	0.11	1.40	0.17

examples of high-temperature, vapor-dominated systems in mountainous terrain and related Cl⁻-rich fluids that undergo extensive lateral migration.

In the above model, where a single parent fluid boils in the subsurface and flows laterally to its low-elevation discharge, some of the calculated advective heat flux (6.5 GW) would be transported by the Cl⁻-rich groundwater, whereas the rest of the heat would be released by Cl⁻-poor steam and gas discharge in the acid sulfate terrains (often at high elevation). The fraction of heat associated with river Cl⁻ flux would be 1.6 GW (~25% of the total), assuming an annual Cl^{-} flux of 50 kt (Table 1) that originates as a parent liquid with 400 mg/l Cl^{-} and cools to the temperature on the boiling-depth curve at the ground surface (~ 95 °C). The remaining 75% of the heat (4.9 GW) would be released with steam and gas discharge in acid sulfate terrains. Because the steam fraction would reach the surface faster than the slowly migrating Cl⁻-rich liquid, it is possible that deep magmatic processes such as intrusion and degassing could be detected more rapidly by monitoring sulfate flux in rivers (e.g. changes in SO_4^{2-} flux in the Yellowstone River) as compared with monitoring of Cl⁻ flux.

7.4. Monitoring strategy

A major motivation for systematic sample collection is to develop an ability to detect changes in the composition and magnitude of the solute flux in response to volcanic unrest and tectonic events. Creating a baseline would also provide the ability to monitor possible flux changes in response to geothermal resource development in areas surrounding YNP (Friedman and Norton, in press). The current river-fluxmonitoring strategy in YNP was designed to detect long-term (annual to decadal) changes in solute flux in response to changes in the hydrothermal system. These Cl⁻ flux measurements since 1983 show no detectable system-wide changes in response to deformation and earthquakes (Ingebritsen et al., 2001; Fournier, 2004).

Much of the current ground-deformation is confined to an area along the northern caldera boundary and the resurgent domes (Fig. 1). The shallowest occurrence of magma as detected by seismic imaging is in the eastern part of the caldera (Miller and Smith, 1999). All these areas drain into the Yellowstone River, with some release into the Gibbon River and, if chemical signals related to this deformation are to be more readily detected, additional sampling locations on the Yellowstone River are required. Currently, much of the solute flux at the Yellowstone River gage at Corwin Springs (Fig. 1) is contributed from Mammoth Hot Springs through the Gardner River and from Yellowstone Lake (Fig. 3a), outside the actively deforming areas. The considerable hydrothermal activity in Yellowstone Lake itself (Morgan et al., 2003; Balistrieri et al., in press) has begun to be monitored by continuous sampling at the lake outlet (Fig. 1).

The current sampling frequency of approximately once per month during base-flow conditions was not sufficient to detect anomalies related to seismic events. If flux changes induced by large earthquakes or thermal disturbances in the geyser basins are to be observed, sampling frequency has to be increased to at least 15min interval.

To detect new magmatic input into the YNP subsurface, measurement of heat transport associated with gas and steam release from soils, as well as heat discharge from fumaroles, might be highly useful. This is because increased steam, gas and heat discharge will likely precede changes in river Cl⁻ flux, particularly if we are correct that many of the Cl⁻-rich waters are far-traveled. Since SO_4^{2-} derives from H₂S, which is mainly transported with the gas phase to the "acid sulfate" areas; it might be that changes in SO_4^{2-} flux will precede changes in Cl⁻ flux in the event of a change in magmatic output.

The large spatial decoupling between Cl⁻ discharge (geyser basins) and heat output (acid sulfate regions) suggests that expansion of satellite and airborne monitoring of thermal features in YNP (Hellman and Ramsey, 2004; Hardy et al., 2005) may be more reliable than current methods to detect and quantify changes in heat (and gas) output over large areas.

8. Conclusions

Data presented in this paper illustrate the large-scale spatial heterogeneity and non-uniform temporal trends of Cl⁻, SO_4^{2-} , HCO_3^{-} , and F^{-} flux through the YNP rivers. Based on these trends we conclude the following:

- Solute fluxes are relatively constant most of the year (base-flow) and increase during the spring runoff in conjunction with increased HCO₃⁻/Cl⁻ and SO₄²⁻/ Cl⁻. An exception is the Firehole River, where solute fluxes change only slightly.
- 2. The total (molar) flux in all rivers decreases in the following order, $HCO_3^->CI^->SO_4^{2-}>F^-$. However, each river is characterized by an identifiable chemical signature, and the distribution of solute flux differs considerably for each one of the measured solutes in each of the rivers. The flux per area differs significantly among the river drainages.

- 3. A larger fraction of the annual solute flux is associated with the spring runoff. In the Yellowstone and Snake Rivers, HCO_3^- and SO_4^{2-} are particularly high, probably because these rivers host lakes in their drainage basins. These anions accumulate during the winter months when the lakes freeze, and are released in the spring when the ice melts.
- 4. Although the CO_2 equivalent (as HCO_3^-) flux through rivers is much larger than other solutes, it is only ~ 1% of the estimated diffuse CO_2 emissions through soils.
- 5. The current sampling strategy is insufficient to track intra-annual changes in river chemistry associated with tectonic or hydrothermal activity. To track such changes, additional gages need to be installed, especially in the Yellowstone River basin, and more frequent and perhaps automated sampling is required.
- 6. It is likely that large-scale heating or cooling of the hydrothermal system would be manifested by changes in the diffuse gas and steam flux.

Acknowledgments

This study would not take place without the tremendous dedication and enthusiasm of the late Irving Friedman who initiated the extensive chloride flux project in Yellowstone NP, and coordinated it for 20 years. We thank Jeff Arnold, Kitty Eneboe, Christine Greve, Paul Miller, Kathleen O'Leary Dave Phillips, and Tara Ross (all from Yellowstone NP) for sampling, Steve Miller (Yellowstone NP) for helping with the coordination of sample collection, and Mark Huebner and Atosa Abedini (USGS) for chemical analysis. Deb Bergfeld, José Virgílio Cruz, Sean Egan, Bill Evans, Fraser Goff, and Steve Ingebritsen are thanked for constructive comments and reviews. This project was funded by the Volcano Hazards Program, U.S. Geological Survey and the National Park Service.

References

- Allen, E.T., Day, A.L., 1935. Hot springs of the Yellowstone National Park. Washington Publication, vol. 466. Carnegie Institute. 525 pp.
- Balistrieri, L.,S., Shanks III, W.C., Cuhel, R.L., Aguilar, C., Klump, J.V., in press. The influence of sublacustrine hydrothermal vents on the geochemistry of Yellowstone Lake. In: Morgan, L.A., (Ed.), Integrated Geoscience Studies in the Greater Yellowstone Area: Volcanic, Hydrothermal and Tectonic Processes in the Yellowstone Geoecosystem. U.S. Geol. Surv. Prof. Pap. 1717.
- Christiansen, R.L., 2001. The Quaternary and Pliocene Yellowstone Plateau volcanic field of Wyoming, Idaho, and Montana. U.S. Geol. Surv. Prof. Pap. P 0729-G, G1–G145.

- Clifton, C.G., Walters, C.C., Simoneit, B.R.T., 1990. Hydrothermal petroleums from Yellowstone National Park, Wyoming, U.S.A. Appl. Geochem. 5, 169–191.
- Dzurisin, D., Savage, J.C., Fournier, R.O., 1990. Recent crustal subsidence at Yellowstone Caldera, Wyoming. Bull. Volcanol. 52, 247–270.
- Dzurisin, D., Yamashita, K.M., Kleinman, J.W., 1994. Mechanisms of crustal uplift and subsidence at the Yellowstone Caldera, Wyoming. Bull. Volcanol. 56, 261–270.
- Ellis, A.J., Wilson, S.H., 1955. The heat from the Weirakei–Taupo thermal region calculated from the chloride output. N. Z. J. Sci. Technol., Sect. B 36, 622–631.
- Fournier, R.O., 1979. Geochemical and hydrologic considerations and the use of enthalpy-chloride diagrams in the prediction of underground conditions in hot-spring systems. J. Volcanol. Geotherm. Res. 5, 1–16.
- Fournier, R.O., 1989. Geochemistry and dynamics of the Yellowstone National Park hydrothermal system. Annu. Rev. Earth Planet. Sci. 17, 13–53.
- Fournier, R.O., 2004. Yellowstone Caldera inflation-deflation and hydrothermal Cl⁻ flux revisited. In: Wanty, R.B., Seal II, R.R. (Eds.), Proceedings of the Eleventh International Symposium on Water–Rock Interaction. A.A. Balkema, Saratoga Springs, New York, pp. 53–58.
- Fournier, R.O., White, D.E., Truesdell, A.H., 1976. Convective heat flow in Yellowstone National Park. Proceedings of the 2nd U.N. Symp. on the Development and Use of Geothermal Resources, San Francisco, pp. 731–739.
- Fournier, R.O., Weltman, U., Counce, D., White, L.D., Janik, C.J., 2002. Results of Weekly Chemical and Isotopic Monitoring of Selected Springs in Norris Geyser Basin, Yellowstone National Park During June–September, 1995. U.S. Geol. Surv. Open File Rep. 02-344.
- Friedman, I., Norton, D.R., 1990. Anomalous chloride flux discharges from Yellowstone National Park. J. Volcanol. Geotherm. Res. 42, 225–234.
- Friedman, I., Norton, D.R., in press. Is Yellowstone losing its steam? Chloride flux out of Yellowstone National Park. In: Morgan, L.A., (Ed.), Integrated Geoscience Studies in the Greater Yellowstone Area: Volcanic, Hydrothermal and Tectonic Processes in the Yellowstone Geoecosystem. U.S. Geol. Surv. Prof. Pap. 1717.
- Gemery, P.A., Shanks III, W.C., Balistrieri, L.S., Lee, G.K., in press. Geochemical data for selected rivers, lake waters, hydrothermal vents and sub-aerial geysers in Yellowstone national Park, Wyoming, and vicinity, 1996–2002. In: Morgan, L.A., (Ed.), Integrated Geoscience Studies in the Greater Yellowstone Area: Volcanic, Hydrothermal and Tectonic Processes in the Yellowstone Geoecosystem. U.S. Geol. Surv. Prof. Pap. 1717.
- Goff, F., Janik, C.J., 2002. Gas geochemistry of the Valles Caldera region, New Mexico and comparisons with gases at Yellowstone, Long Valley and other geothermal systems. J. Volcanol. Geotherm. Res. 116, 299–323.
- Gooch, F.A., Whitfield, J.E., 1888. Analyses of waters of the Yellowstone National Park, with an account of the methods of analysis employed. U.S. Geol. Surv. Bull. B-0047, 84.
- Gunter, B.D., Musgrave, B.C., 1966. Gas chromatographic measurements of hydrothermal emanations at Yellowstone National Park. Geochim. Cosmochim. Acta 30, 1175–1189.
- Hardy, C.C., Heasler, H.P., Queen, L.P., Jaworowski, C., 2005. Mapping active thermal features in Yellowstone National Park using airborne multi-spectral remote sensing data with dynamic calibrations. Geol. Soc. Am. Abstr. Prog., Denver 37 (7), 127.

- Hellman, M.J., Ramsey, M.S., 2004. Analysis of hot springs and associated deposits in Yellowstone National Park using ASTER and AVIRIS remote sensing. J. Volcanol. Geotherm. Res. 135, 195–219.
- Husen, S., Wiemer, S., Smith, R.B., 2004a. Remotely triggered seismicity in the Yellowstone National Park region by the 2002 M_w =7.9 Denali Fault earthquake, Alaska. Bull. Seismol. Soc. Am. 94, 317–331.
- Husen, S., Taylor, R., Smith, R.B., Healser, H., 2004b. Changes in geyser eruption behavior and remotely triggered seismicity in Yellowstone National Park produced by the 2002 M 7.9 Denali Fault earthquake, Alaska. Geology 32, 537–540.
- Ingebritsen, S.E., Sorey, M.L., 1988. Vapor-dominated zones within hydrothermal systems: evolution and natural state. J. Geophys. Res. 93, 13,635–13,655.
- Ingebritsen, S.E., Galloway, D.L., Colvard, E.M., Sorey, M.L., Mariner, R.H., 2001. Time-variation of hydrothermal discharge at selected sites in the western United States: implications for monitoring. J. Volcanol. Geotherm. Res. 111, 1–23.
- Kennedy, B.M., Reynolds, J.H., Smith, S.P., Truesdell, A.H., 1987. Helium isotopes; Lower Geyser Basin, Yellowstone National Park. J. Geophys. Res. 92, 12,477–12,489.
- Kharaka, Y.K., Thordsen, J.J., White, L.D., 2002. Isotope and chemical compositions of meteoric and thermal waters and snow from the greater Yellowstone National Park Region. U.S. Geol. Surv. Open File Rep. 02-194. 75 pp.
- Love, J.D., Good, J.M., 1970. Hydrocarbons in thermal areas, northwestern Wyoming. U.S. Geol. Surv. Prof. Pap. 644-B (23 pp.).
- Lowenstern, J.B., Heasler, H., Smith, R.B., 2003. Hydrothermal disturbances at the Norris Geyser Basin, Yellowstone National Park (USA) in 2003. Eos Trans. AGU 84 (46) (Fall Meet. Suppl., Abstract V31B-05).
- Lowenstern, J.B., Smith, R.B., Hill, D.P., 2006. Monitoring supervolcanoes: geophysical and geochemical signals at Yellowstone and other large caldera systems. Philos. Trans. R. Soc. Lond., A 364, 2055–2072.
- Marler, G.D., White, D.E., 1975. Seismic geyser and its bearing on the origin and evolution of geysers and hot springs of Yellowstone National Park. Geol. Soc. Am. Bull. 86, 749–759.
- Miller, D.S., Smith, R.B., 1999. P and S velocity structure of the Yellowstone volcanic field from local earthquake and controlled source tomography. J. Geophys. Res. 104, 15,105–15,121.
- Morgan, L.A., Shanks, W.C., Lovalvo, D.A., Johnson, S.Y., Stephenson, W.J., Pierce, K.L., Harlan, S.S., Finn, C.A., Lee, G., Webring, M., Schulze, B., Dühn, J., Sweeney, R., Balistrieri, L., 2003. Exploration and discovery in Yellowstone Lake: results from high-resolution sonar imaging, seismic reflection profiling, and submersible studies. J. Volcanol. Geotherm. Res. 122, 221–242.
- Muffler, L.J.P., White, D.E., Truesdell, A.H., 1971. Hydrothermal explosion craters in Yellowstone National Park. Geol. Soc. Am. Bull. 82, 723–740.
- Newhall, C.G., Dzurisin, D., 1988. Historical unrest at large calderas of the world. U.S. Geol. Surv. Bull. 1855 (1108 pp.).
- Norton, D.R., Friedman, I., 1985. Chloride flux out of Yellowstone National Park. J. Volcanol. Geotherm. Res. 26, 231–250.
- Pierce, K.L., Adams, K.D., Sturchio, N.C., 1991. Geologic setting of the Corwin Springs known geothermal resources area mammoth

hot springs area in and adjacent to Yellowstone National Park. In: Sorey, M.L. (Ed.), Effects of Potential Geothermal Development in the Corwin Springs Known Geothermal Resources Area, Montana, on the thermal features of Yellowstone National Park. U.S. Geol. Surv. Water Res. Invest. Rep. 91-4052, pp. Cl–C37.

- Pitt, A.M., Hutchinson, R.A., 1982. Hydrothermal changes related to earthquake activity at Mud Volcano, Yellowstone National Park, Wyoming. J. Geophys. Res. 87, 2762–2766.
- Rowe, J.J., Fournier, R.O., Morey, G.W., 1973. Chemical analysis of thermal waters in Yellowstone National Park, Wyoming, 1960– 1965. U.S. Geol. Surv. Bull. 1303 (31 pp.).
- Rye, R.O., Truesdell, A.H., 1993. The question of recharge to the geysers and hot springs of Yellowstone National Park. U.S. Geol. Surv. Open File Rep. 93-384. 40 pp.
- Sorey, M.L., Colvard, E.M., Nimick, D.A., Shields, R.R., Thordsen, J.J., Ambats, G., 1991. In: Sorey, M.L. (Ed.), Effects of Potential Geothermal Development in the Corwin Springs Known Geothermal Resources Area, Montana, on the thermal features of Yellowstone National Park. U.S. Geol. Surv. Water Res. Invest. Rep. 91-4052, pp. G1–G41.
- Symonds, R.B., Gerlach, T.M., Reed, M.H., 2001. Magmatic gas scrubbing: implications for volcano monitoring. J. Volcanol. Geotherm. Res. 108, 303–341.
- Theriot, E.C., Fritz, S.C., Gresswell, R.E., 1997. Long-term limnological data from the larger lakes of Yellowstone National Park. J. Arct. Alp. Res. 29, 304–314.
- Thompson, J.M., DeMonge, J.M., 1996. Chemical analyses of hot springs, pools, and geysers from Yellowstone National Park, Wyoming, and vicinity, 1980–1993. U.S. Geol. Surv. Open File Rep. 96-0068. 66 pp.
- Truesdell, A.H., Fournier, R.O., 1976. Conditions in the deeper parts of hot spring systems of Yellowstone National Park, Wyoming. U.S. Geol. Surv. Open File Rep. 76-428. 29 pp.
- Truesdell, A.H., Nathenson, M., Rye, R.O., 1977. The effects of subsurface boiling and dilution on the isotopic compositions of Yellowstone thermal waters. J. Geophys. Res. 82, 3964–3704.
- Waite, G.P., Smith, R.B., 2002. Seismic evidence for fluid migration accompanying subsidence of the Yellowstone Caldera. J. Geophys. Res. 107, 2177. doi:10.1029/2001JB000586.
- Werner, C., Brantley, S., 2003. CO₂ emissions from the Yellowstone volcanic system. Geochem. Geophys. Geosyst. 4, 1061. doi:10.1029/2002GC000473.
- White, D.E., Muffler, L.J.P., Truesdell, A.H., 1971. Vapor-dominated hydrothermal systems compared with hot-water systems. Econ. Geol. 66, 75–97.
- Wicks, C.W., Thatcher, W.R., Dzurisin, D., 1998. Migration of fluids beneath Yellowstone Caldera inferred from satellite radar interferometry. Science 282, 458–462.
- Wicks, C.W., Thatcher, W., Dzurisin, D., Svarc, J., 2006. Uplift, thermal unrest, and magma intrusion at Yellowstone Caldera. Nature 440, 72–75 doi: 10.1038.
- Xu, Y., Schoonen, M.A.A., Nordstrom, D.K., Cunningham, K.M., Ball, J.W., 1998. Sulfur geochemistry of hydrothermal waters in Yellowstone National Park: I. The origin of thiosulfate in hot spring waters. Geochim. Cosmochim. Acta 62, 3729–3743.