Research paper

River solute fluxes reflecting active hydrothermal chemical weathering of the Yellowstone Plateau Volcanic Field, USA

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A R T I C L E   I N F O

Article history:
Received 24 March 2010
Accepted 3 July 2010
Editor: J.D. Blum

Keywords:
Yellowstone
Chemical weathering
Hydrothermal
Magmatic
River chemistry
Denudation

A B S T R A C T

In the past few decades numerous studies have quantified the load of dissolved solids in rivers to determine chemical weathering rates in orogenic belts and volcanic areas, mainly motivated by the notion that over timescales greater than ~100 kyr, silicate hydrolysis may be the dominant sink for atmospheric CO2, creating a feedback between climate and weathering. Here, we report the results of a detailed study during water year 2007 (October 1, 2006 to September 30, 2007) in the major rivers of the Yellowstone Plateau Volcanic Field (YPVF) which hosts Earth’s largest “restless” caldera and over 10,000 thermal features. The chemical compositions of rivers that drain thermal areas in the YPVF differ significantly from the compositions of rivers that drain non-thermal areas. There are large seasonal variations in river chemistry and solute flux, which increases with increasing water discharge. The river chemistry and discharge data collected periodically over an entire year allow us to constrain the annual solute fluxes and distinguish between low-temperature weathering and hydrothermal flux components. The TDS flux from Yellowstone Caldera in water year 2007 was 93 t/km²/year. Extensive magma degassing and hydrothermal interaction with rocks accounts for at least 82% of this TDS flux, 83% of the cation flux and 72% of the HCO3− flux. The low-temperature chemical weathering rate (17 t/km²/year), calculated on the assumption that all the Cl− is of thermal origin, could include a component from low-temperature hydrolysis reactions induced by CO2 ascending from depth rather than by atmospheric CO2. Although this uncertainty remains, the calculated low-temperature weathering rate of the young rhyolitic rocks in the Yellowstone Caldera is comparable to the world average of large watersheds that drain more soluble carbonates and evaporates but is slightly lower than calculated rates in other, less-silicic volcanic regions. Long-term average fluxes at Yellowstone are likely ~20% higher than those in the abnormally dry water year 2007, but the protocol used in this study can be easily adaptable to track future changes in low-temperature weathering and hydrothermal flux components, which could provide better monitoring of magmatic unrest.

1. Introduction

Chemical weathering of large watersheds (>100 km²) is a major process influencing landscape evolution, nutrient supply to soils and streams, and global geochemical cycles. In the past few decades research on chemical weathering has mainly focused on using the load of dissolved solids in rivers as a proxy for rock weathering (e.g. Drever and Clow, 1995; White and Blum, 1995; Gaillardet et al., 1999; Dupré et al., 2003; Meybeck, 2003; Tipper et al., 2006; Hren et al., 2007). A primary motivation for many of these studies relates to the notion that over timescales greater than the residence time of bicarbonate (HCO3−) in seawater (~100 kyr), silicate hydrolysis may be the dominant sink for atmospheric CO2, thus creating a feedback between climate and weathering (Berner et al., 1983; Raymo and Ruddiman, 1992; Kump et al., 2000; Gíslason et al., 2008).

While weathering of silicate rocks from the world’s major rivers has been shown to play a strong role in global consumption of CO2, global compilations (Gaillardet et al., 1999) did not include data from rivers draining active magmatic provinces, where silicate hydrolysis is likely induced to some degree by acid gases emanating from a deep magma (e.g. Giggenbach, 1984, 1988; Chiodini et al., 1991; Christopherson, 2000; Taran, 2009) rather than by atmospheric CO2. Several studies have quantified chemical weathering rates in volcanic systems (Gíslason et al., 1996; Louvat and Allègre, 1997, 1998; Varekamp and Thomas, 1998; Stefansson and Gíslason, 2001; Dessert et al., 2003; Rad et al., 2006, 2007; Goldsmith et al., 2008; Gíslason et al., 2009; Goldsmith et al., 2010), but only recently, the role of magmatic gases and high-temperature water–rock interactions were incorporated into the calculations (Dessert et al., 2009). In all these studies, the flux of major elements originating from high-temperature reactions was calculated based on the assumption that most, or all of the chlorine in...
the rivers is derived from precipitation. However, such assumptions are likely to introduce errors, because a significant fraction of the chlorine in these systems could be of magmatic origin.

This study was carried out with the objective of characterizing and quantifying water–rock interaction and chemical weathering rates and riverine fluxes of major ions in the Yellowstone Plateau Volcanic Field (YPVF) (Fig. 1). More specifically, our goals are to: (1) determine the magnitude of chemical weathering induced by atmospheric CO₂ relative to that induced by high-temperature rock interaction with magmatic gases, (2) estimate the denudation rates across Yellowstone Caldera, and (3) provide a baseline against which fluxes during periods of increased magma degassing and volcanic unrest can be compared.

The YPVF is a prime location to address the above goals because (1) all the major rivers have gages (Fig. 1) (U.S. Geological Survey National Water Information System) and a well established sampling protocol (Friedman and Norton, 2007; Hurwitz et al., 2007a,b) providing high quality water discharge records and precise solute flux determinations, characterization of spatial patterns, and quantification of temporal trends (2) high emission rates of magmatic gases, mainly CO₂ (Werner and Brantley, 2003; Werner et al., 2008) imply that the underlying magmatic system is active and extensively degassing; (3) geochemical and thermodynamic models of thermal fluid composition (Truesdell and Fournier, 1976; Fournier, 1989; Lowenstern and Hurwitz, 2008) and detailed descriptions of hydrothermal alteration minerals from research drill holes (e.g. Keith and Muffler, 1978; Sturchio et al., 1986) provide constraints on the high temperature water–rock interaction (4) Corrections for atmospheric deposition of major elements are not required because precipitation in the area is extremely dilute and the contribution of precipitation-derived solutes to the river load is negligible (Miller and Drever, 1977; Zelt et al., 1998; Kharaka et al., 2002; Hurwitz et al., 2007a).

2. Geologic setting

The YPVF hosts Earth’s largest “restless” caldera (Newhall and Dzurisin, 1988; Christiansen, 2001; Lowenstern et al., 2006), containing over 10,000 thermal features (Fournier, 1989) and covering about 6500 km² at an average elevation of approximately 2400 m above sea level (Fig. 1). It has been a center for rhyolitic volcanism during the
past 2.2 Ma with three cataclysmic caldera-forming events at 2.1, 1.3, and 0.6 Ma; each preceded and succeeded by large eruptions of rhyolitic lava. Shortly after the last major eruption which formed the Yellowstone Caldera, two resurgent domes emerged and three relatively short episodes of rhyolitic volcanism at ~150, 110, and 70 kyr filled large volumes of the caldera. During this time there was limited basaltic volcanism outbreak of the Yellowstone Caldera margin (Christiansen, 2001).

The YPVF comprises two areas with distinct lithologies; a zone outside Yellowstone Caldera consisting mostly of welded rhyolitic ash-flow tuffs and associated small volume rhyolitic and basaltic lava flows and the area within Yellowstone Caldera consisting mainly of very large volume rhyolitic lava flows. The bulk of the surficial volcanic rocks (~95 vol.%) are high silica rhyolite (generally >75% SiO2). YPVF is surrounded by Tertiary extrusive and intrusive rocks predominantly of andesitic composition of the Absaroka group, and by Paleozoic sedimentary rocks and Precambrian metamorphic rocks (Christiansen, 2001). Mammoth Hot Springs which covers an area of ~4 km² in the northern part of the plateau (Fig. 1) is one of the world’s largest sites of active travertine deposition. The underlying thick sequence of Mesozoic sedimentary rocks includes limestone, dolomite, and gypsum-bearing shales (Pierce et al., 1991).

Geophysical data suggest that partially molten magma underlies much of the 0.6-Ma Yellowstone caldera at depths ranging from about 5 to 10 km, and possibly shallower beneath portions of the eastern half of the caldera (Husen et al., 2004). This magma is associated with a heat output of 5–6 GW (Fournier, 1989; Friedman and Norton, 2007), abundant seismicity (Waitt and Smith, 2002), cycles of ground surface uplift and subsidence (e.g. Wicks et al., 2006; Chang et al., 2007), and extensive degassing (Werner and Brantley, 2003; Werner et al., 2008).

Thermal areas at YPFV contain waters of neutral-chloride, acid-sulfate and mixed compositions. Thermal features characterized by neutral to slightly alkaline water, relatively high concentrations of Cl− and SiO2 and siliceous sinter deposition are mainly found in geyser basins along the Firehole and Gibbon Rivers (Fig. 1). Acid-sulfate areas are characterized by fumaroles and mud pots with limited liquid-water discharge, low chloride, and high sulfate concentrations (White et al., 1971). They 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).

3. Climate and hydrology of the Yellowstone Plateau

Snow composes a substantial part of the precipitation at the YPVF with an annual average of 180 cm water equivalent; occurring mainly between October and April with maxima in January. Rain is distributed throughout the year with maxima in May and June and an average total of 38 cm (U.S. National Climate Data Center). Extremely low winter temperatures, with a minimum average monthly temperature of −12.1 °C in January causes lakes and some of the smaller tributaries to freeze. Following ice thaw and snowmelt in May there is a rapid increase in discharge peaking in late May–June. Discharge then decreases over 2–3 months to base flow conditions (Fig. 2a).

Four major rivers drain most of YPVF: the Madison and Yellowstone Rivers east of the continental divide and the Snake, and Falls Rivers west of the divide (Fig. 1). The Yellowstone River above the gage at Corwin Springs (YYCO in Fig. 1) has the largest drainage area (Supplementary material — Table 1) capturing flow from Yellowstone Lake (YYFB), several areas of acid-sulfate basins along the segment of the river between Yellowstone Lake and Tower Junction (YOTJ), the Lamar River (YLAM) which mainly drains andesites of the Absaroka group and Precambrian metamorphic rocks, and the Gardner River (YGAR) which captures the discharge of many springs along the Norris–Mammoth corridor and the travertine-depositing Mammoth Hot Springs through Boiling River (Hurwitz et al., 2007a). The Madison River includes the flow from the Firehole River (YFIR), which drains the Upper, Midway and Lower Geyser Basins, and the Gibbon River (YGIB), which drains the Norris and Gibbon Geyser Basins (Mccleskey et al., 2010) (Fig. 1). Together, the Firehole and Gibbon Rivers drain 97% of the Madison River drainage area above its gage near West Yellowstone, Montana (YMAD in Fig. 1), and their combined annual water discharge for water year 2007 accounts for 92% of the Madison River discharge. Overall, the watersheds comprised of quaternary volcanics are characterized by high volumes of groundwater circulation and thus, advection is the dominant mechanism for mass and energy transport in the hydrothermal system (Gardner et al., 2010).

4. Methods

4.1. Sampling and analytical procedures

During water year 2007 (October 1, 2006 to 30 September, 2007) water samples from the Yellowstone River drainage were collected from the Yellowstone River at Corwin Springs (YYCO), Fishing Bridge (YYFB), and Tower Junction (YYTJ), and from the Lamar River (YLAM) near Tower Junction, and from the Gardner River (YGAR) near Mammoth (Fig. 1). Samples from the Madison River drainage were collected from the Firehole (YFIR) and Gibbon (YGIB) rivers above their confluence with the Madison River, near Madison Junction. Samples were collected in high-density polyethylene bottles and filtered in the field with a 0.45 µm filter. One bottle from each sample was acidified with nitric acid within 24 h for cation analysis.

Samples were collected once per month between October and March, twice a month in April and September, and once a week between May and August following snowmelt when water discharge rates are at their highest. A maximum of 28 samples were collected from each river, but the actual number was less in most cases; in particular, many samples from the Yellowstone River at Fishing Bridge and Tower Junction and from the Lamar River are missing (Supplementary material — Table 1).

Concentrations of Cl−, F−, and SO4− were determined using a Dionex ion chromatograph ICS-2000 and cation concentrations were determined using a Thermo Scientific ICAP 6000 inductively coupled plasma atomic emission spectrometer (ICP-AES). Analytical errors for these constituents are typically <5%. Total alkalinity as HCO3− was determined on stored samples, usually within several months after collection. Ten milliliters of sample were titrated with 0.05 N sulfuric acid to the bicarbonate end-point. The analytical error in the determined alkalinity concentrations is roughly ±10%. All the analyses were carried out at the U.S. Geological Survey laboratories in Menlo Park, California. The charge balance between cations and anions is better than 10% for most samples (Supplementary material — Table 1).

Stream discharge at the time of sampling was obtained from the gages at individual sites (U.S. Geological Survey, National Water Information System — Supplementary material — Table 1). The automated 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.

4.2. Solute flux determinations

The instantaneous discharge of each dissolved ion was calculated by multiplying the sample concentration by the river discharge at the time of sample collection. The annual discharge of each ion was derived by integrating the instantaneous discharge throughout the
year. The gaging station on the Yellowstone River at Tower Junction (YYTJ — Fig. 1) was operational only between 1983 and 1986. To derive the discharge in water year 2007, we calculated the ratio between the monthly average discharge at Tower Junction and the monthly average discharge of the Yellowstone River at Fishing Bridge (YYFB) for each month during the 1983–1986 period. We then multiplied the measured monthly discharge at Fishing Bridge by the calculated month-specific ratio, which ranged from 1.3 to 2.1.

We estimate that the error in river discharge measurements (<5%), analytical errors, and the error associated with the integration of solute discharge measurements between consecutive measurements result in less than 10% error in the estimate of annual discharge of ions for locations in which at least 20 samples were collected and up to 20% error in locations in which less than 10 samples were collected.

The flux of major elements and of total cations and TDS (t/km²/year) were calculated for each drainage basin and for the Yellowstone Caldera by dividing the annual discharge of the solute by the area of the drainage basin or the caldera (Table 1). The calculated fluxes from Yellowstone Caldera include the sums from the Yellowstone River at Fishing Bridge and Tower Junction and from The Firehole and Gibbon Rivers (Fig. 1). The fluxes from Tower Junction presented in Table 1 were calculated by subtracting the weathering rates from Fishing Bridge to represent the rate from the area between Yellowstone Lake and Tower Junctions, which is occupied by several vapor-dominated acid-sulfate basins.

5. River chemistry and solute flux

5.1. Chemical composition

Major-element concentrations in the Yellowstone and Madison River watersheds for water year 2007 are presented in the Supplementary material — Table 1. The pH of the samples at the time of collection ranged between 7.5 and 8.0 and water temperatures ranged between 2 °C in January and 26 °C in July.

Water discharge and the associated solute concentrations, fluxes, and compositions varied throughout the year. Water chemistry associated with the high runoff period between late April and mid-June differs significantly from the composition of the base flow. The ratios of HCO₃⁻, SO₄²⁻, Ca²⁺, and Mg²⁺ to Cl⁻ increase during the high runoff period. The ratio increase is significantly greater in rivers with a high runoff component (Yellowstone River at Corwin Springs and the
Tower Junction have a higher K+/Na+ compared with waters of the compared with divalent cations. Waters from the Gibbon River and Caldera and Norris Geyser Basin, which are enriched with monovalent chloride thermal springs from the major geyser basins in Yellowstone located to the west and northwest of the caldera (Fig. 1) and neutral-carbonates and gypsum from Mammoth Hot Springs area (Fig. 3a).

Bicarbonate (HCO$_3^-$) is the main anion in all YPVF rivers on a molar basis, but Cl$^-$ is nearly as abundant in the Firehole and Gibbon Rivers (Fig. 5). The large compositional variability of water at Corwin Springs and the Gardner River (Figs. 4 and 5) is mainly due to seasonal effects (Fig. 2). The compositions trend from a HCO$_3^-$-rich end-member during spring runoff to a more Cl$^-$ and SO$_4^{2-}$-enriched thermal composition during base flow conditions (Figs. 2 and 5). The waters of Mammoth Hot Springs (Fig. 1) that drain large travertine terraces, and which flow into the Gardner River are controlled to a first order by gypsum and calcite precipitation–dissolution reactions; they are supersaturated with respect to calcite (Kharaka et al., 1990) and the molar Ca/SO$_4$ is ~1. Waters at Tower Junction are relatively enriched with SO$_4$ which has been shown to be derived from microbial sulfur oxidation to sulfuric acid in near-surface environments (Nordstrom et al., 2009; Shock et al., 2010).

The relatively high molar Na/HCO$_3$ ratios in waters that drain thermal areas of YPVF are unusual in river systems. The high average molar ratios of Na/HCO$_3$ (1.9) and Na/(K + Ca + Mg) (6.7) in the Firehole and Gibbon Rivers (1.9) imply that about 50% of the Na$^+$ in the rivers is not derived from the interaction of silicate rocks with carbonic acid. In these rivers the remaining 50% of the Na$^+$ is balanced by Cl$^-$, which reflects a NaCl component formed deep in the hydrothermal system.

5.2. Solute flux and denudation rates

Solute flux of major elements from the rivers in the Yellowstone and Madison River watersheds are presented in Table 1. We have not corrected for atmospheric deposition of major elements, because the contribution of precipitation-derived Cl$^-$ was calculated to be <4% (Hurwitz et al., 2007a) and based on concentrations of major cations in local precipitation (Kharaka et al., 2002), we estimate that the represent a mixture of cold carbonate and non-carbonate springs (C and N in Fig. 4).

| Table 1 Solute flux and low-temperature chemical weathering (t/km$^2$/year) from rivers in Yellowstone and in other volcanic regions. |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| River           | Ca  | Na  | K   | Mg  | Li  | HCO$_3^-$ | SO$_4^{2-}$ | Cl  | F   | B   |
| Corwin Springs  | 4   | 4   | 1   | 1   | 0.02| 18          | 6            | 2   | 0.07| 5   |
| Gardiner        | 13  | 6   | 2   | 4   | 0.06| 40          | 24           | 6   | 0.14| 6   |
| Fishing Bridge  | 2   | 3   | 1   | 1   | 0.02| 12          | 3            | 2   | 0.03| 3   |
| Tower Junction  | 5   | 17  | 3   | 1   | 0.10| 33          | 20           | 10  | 0.47| 18  |
| Lamar           | 2   | 1   | 0   | 1   | 0.00| 14          | 1            | 1   | 0.00| 3   |
| Firehole        | 2   | 29  | 3   | 0   | 0.25| 45          | 4            | 23  | 0.26| 29  |
| Gibbon          | 2   | 18  | 3   | 0   | 0.14| 31          | 7            | 15  | 0.22| 19  |
| Yellowstone     | 3   | 16  | 2   | 1   | 0.11| 33          | 9            | 11  | 0.22| 16  |

Low-temperature chemical weathering rates

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<th>Ca</th>
<th>Na</th>
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<th>SO$_4^{2-}$</th>
<th>Cl</th>
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Chemical weathering rates in other volcanic regions

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Numbers in parentheses are the percentage of the low-temperature component. An asterisk in the parentheses indicates that separate low temperature and thermal components were not calculated, and a question mark indicates that separate components were calculated but their percentages were not provided.
contribution of precipitation-derived cations to the river load is less than 5%.

The calculated cation and TDS fluxes from the Yellowstone caldera for water year 2007 are 27 and 93 t/km²/year, respectively. These values are probably lower than mean annual solute fluxes, because the annual water discharge through the Yellowstone and Madison Rivers was only 72% and 81%, respectively of the annual average for water years 1990 to 2007 (U.S Geological Survey National Water Information System), and previous studies have shown a considerable positive correlation between riverine discharge and mass flux (Ingebritsen et al., 2001; Friedman and Norton, 2007; Hurwitz et al., 2007a). Based on the cation/anion and TDS/anion mass ratios in Yellowstone River at Corwin Springs for water year 2007 of 0.4 and 1.7, respectively, and the anion mass discharge rate in water years 2002 to 2007 (Hurwitz et al., 2007b), we calculated a six-year (2001–2007) average cation and TDS fluxes of 27 and 110 t/km²/year, respectively.

The highest TDS fluxes are from the intra-caldera drainages of Yellowstone River at Tower Junction, the Firehole and Gibbon Rivers, and from the extra-caldera drainage of the Gardner River (Table 1). The intra-caldera waters are characterized by high fluxes of Na+, Li+, HCO₃⁻, Cl⁻, F⁻, B, and SiO₂, and low fluxes of Mg²⁺ compared with extra-caldera waters (Table 1). The Yellowstone River at Tower Junction, which drains most of the acid-sulfate areas in the YPVF, is also characterized by a high SO₄²⁻ flux, which is comparable to the flux from the Gardner River that drains gypsum-rich sedimentary rocks in the Mammoth Hot Springs area.

The denudation rate of Yellowstone Caldera (2900 km²) was calculated assuming that only the cations and SiO₂ are dissolved from the solid rock. We divide the sum of the cation and SiO₂ fluxes from the caldera (39 t/km²/year — Table 1) by the density of rhyolite 2300 kg/m³ and calculate a denudation rate of 1.7 cm/kyr resulting from chemical erosion. To the extent that any cations or SiO₂ are derived from magmatic fluids, the denudation rate would be lower.

Estimates of physical erosion rates can be obtained from sediment discharge measurements that were made at Yellowstone River at Corwin Springs between 1985 and 1992 (U.S. Geological Survey National Water Information System) and in the Gibbon River during several weeks throughout 2000 and 2001 (Wright and Zeit, 2003). At Corwin Springs, rates of physical weathering and chemical (TDS)
weathering are of similar magnitude, whereas in the Gibbon River physical erosion rates are lower than the chemical erosion rate. This is atypical of most river systems with significant topography where physical erosion rates are generally much greater than chemical erosion rates, and demonstrates that the magnitude of chemical erosion in the YPVF is very high.

6. Discussion

6.1. Atmospheric CO2 vs. acid gas-hydrothermal weathering

A major goal of many chemical weathering studies in active orogenic belts and volcanic regions is to quantify the mass of atmospheric CO2 consumed by reaction with silicate rocks. The only surface exposure of the more soluble carbonate rocks is in Mammoth Hot Springs (Fig. 1) which is outside the Yellowstone Caldera. Sedimentary units underlying the Yellowstone volcanics are most likely metamorphosed at high temperatures and thus, in contrast to most studies of chemical weathering, separating contributions from carbonates and silicates is not required. As inferred from several lines of evidence presented below, the fraction of solute fluxes originating from chemical weathering induced by atmospheric CO2 in thermal areas of the YPVF is minor.

6.1.1. Hydrolysis by magma-derived acid gases

In thermal areas draining Yellowstone Caldera, only 48% of the cation concentrations Tower Junction, 44% in the Firehole River, and 45% in the Gibbon River are charge balanced by HCO$_3^-$, whereas 82% of the cations in the Lamar River which drains non-thermal areas outside Yellowstone Caldera are balanced by HCO$_3^-$. Charge balance considerations indicate that for the Firehole and Gibbon Rivers, 38% and 39% of the cation concentrations could be balanced by Cl$^-$, and in Tower Junction 17% and 24% could be balanced by SO$_4^{2-}$ and Cl$^-$, respectively. This implies that in addition to rock hydrolysis by carbonic acids, a significant amount of the cations in the thermal waters are derived from the high-temperature dissolution of rocks at depth by sulfuric and/or hydrochloric acid. These observations are consistent with a study in the Kamchatka Peninsula, where it was determined that high-temperature weathering flux is induced almost equally by carbonic, sulfuric, and hydrochloric acids (Dessert et al., 2009). Thus, river compositions represent an integration of extensive water–gas–rock interaction over a considerable depth range with variable pressure, temperature, phase distribution, and lithology and varying degrees of surficial chemical erosion (Truesdell and Fournier, 1976; Fournier, 1989; Lowenstern and Hurwitz, 2008).

6.1.2. Mixing of thermal and low-temperature components

The solute contribution from a hydrothermal source can be derived for each of the studied rivers based on the assumption that all the discharged Cl$^-$ in the rivers is derived from a thermal source, consistent with the estimate that only ~4% of the Cl$^-$ is derived from precipitation (Hurwitz et al., 2007a). This is consistent with estimates that the maximum annual thermal Cl load for the major rivers in the YPVF is 94% of the total load Friedman and Norton (2007). Fournier (1989) proposed that a mixture of about 0.2–0.4% chloride liberated from a crystallizing magma (thermal source) with 99.6–99.8% meteoric water could account for all the chloride discharged by the Yellowstone hot springs. The non-thermal Cl$^-$ component derived from precipitation and leaching of volcanic rocks was estimated to have a concentration of 1–2 mg/l (Fournier, 1989). We further assume that riverine solute discharge can be approximated by the mixing of two end-members, one thermal and the other derived from low-temperature chemical weathering.

We define the composition of the low-temperature end-member for each river by extrapolating the linear fit in the ion-Cl$^-$ relation to the intercept where Cl$^-$ concentration equals zero. This procedure is illustrated for the Firehole and Gibbon Rivers where the data are spread on a linear trend (Fig. 6). The Na$^+$/Cl$^-$ and HCO$_3^-$/Cl$^-$ ratios in these rivers are similar to the ratios in thermal neutral chloride waters with the highest HCO$_3^-$/Cl$^-$ (Fig. 6a,b), further implying that these solutes are mainly derived from high-temperature water–rock interaction. The waters of the Firehole and Gibbon Rivers have higher K$^+$/Cl$^-$, SO$_4^{2-}$/Cl$^-$, and Ca$^{2+}$/Cl$^-$ ratios compared with the thermal springs (Fig. 6c–e) resulting from input of some acid-sulfate water along with moderate-temperature thermal waters richer in Ca$^{2+}$.

The linear relations are quite robust and typically $r^2 \geq 0.8$ for solutes in all the rivers; exceptions include the Mg$^{2+}$/Cl$^-$ in the Firehole and Gibbon Rivers, which is due to the very low Mg$^{2+}$ concentrations and the relations of most ions with Cl$^-$ in the Yellowstone River at Fishing Bridge, because of the very small range of Cl$^-$ concentrations. The intercepts for SO$_4^{2-}$/Cl$^-$, and Ca$^{2+}$/Cl$^-$ are slightly negative probably resulting from non-conservative solute behavior in Yellowstone Lake, such as SiO$_2$ uptake by diatoms, or complexities in the input of the acid-sulfate component. In these cases, we assigned a value of 0 to the intercept which implies that all the SO$_4^{2-}$ and SiO$_2$ at Fishing Bridge and all the SO$_4^{2-}$ at Tower Junction are of thermal origin.

Based on the calculated concentration of each dissolved ion at Cl$^- = 0$, we calculated the percentage of the low-temperature component for each sample collected and for the annual average flux (Figs. 7 and 8 and Table 1). The percentage of the low-temperature component changes throughout the year and it is more significant at Corwin Springs with large water discharge variations (Fig. 7) than in the Firehole Rivers where discharge variations are relatively small (Fig. 8). A large fraction of the low-temperature component is discharged during the high runoff period between April and June. Our calculations suggest that only 9%, 25%, and 28% of the HCO$_3^-$ in the Firehole River, Gibbon River, and Yellowstone Caldera respectively, originate from low-temperature chemical weathering (Table 1). The low values for the Firehole and Gibbon Rivers are supported by the $^{14}$C concentration (0.186 times modern) in a sample collected from the Madison...
River in September 2004, 2 km downstream from the confluence of the Firehole and Gibbon Rivers (Fig. 1) showing that only 17% of the carbon is derived from atmospheric CO$_2$. This determination is based on a total dissolved inorganic carbon (DIC) concentration of 2.46 mM, $\delta^{13}$C$_{DIC} = +0.02$‰, and 14C concentration in air of about 1.07 times modern.

The above calculated percentages of the low-temperature HCO$_3^-$ are probably maxima because: 1) Non-carbonate cold springs on the margin of the YPVF (Fig. 1) contain some magmatic CO$_2$ as inferred from carbon isotopes (Evans et al., 2006), 2) the hydrothermal end-member probably degasses CO$_2$ between the subsurface reservoir and the spring (Fournier, 1989) and reacts upon cooling with rocks (Bischoff and Rosenbauer, 1996), and 3) the calculated percentage of atmospheric 14C in the river sample could reflect some water–air CO$_2$ exchange. The calculated HCO$_3^-$ of thermal origin is not necessarily all magmatic because carbon isotopes suggest that 30–50% of the CO$_2$ emitted in the YPVF could be derived from metamorphic pre-Tertiary metasediment basement rocks (Werner and Brantley, 2003).

The mixing calculations also demonstrate that most of the monovalent cations in the intra-caldera waters are derived from hydrothermal–rock interactions; For example, 8% and 12% of the Na$^+$ in the Firehole River and Gibbon River, respectively, are derived from low-temperature hydrolysis, whereas a much higher proportion of the Mg$^{2+}$ and Ca$^{2+}$ are derived from low-temperature weathering (Table 1). Such a composition is consistent with extensive hydrothermal interactions with magmatic/volcanic rocks (Giggenbach, 1984, 1988).

6.2. Comparison with chemical weathering rates in other watersheds

Comparing the calculated fluxes of solutes from the YPVF to rates in other active volcanic regions is complicated, because the different
datasets represent a range of methods that provide estimates with highly variable temporal precision and accuracy. The dataset of YPVF river solute discharge relies on numerous samples throughout the year that account for large seasonal variations and precise water discharge measurements (error <5%), which result in relatively small errors (≤10% except for Tower Junction) associated with the calculation of solute flux.

Another significant source of inconsistency in the comparisons is the method applied to separate solutes originating from hydrothermal–rock interaction from those originating from low temperature hydrolysis induced by atmospheric CO₂. In some chemical weathering studies, corrections for a thermal component were not made, and thus, low-temperature chemical weathering rates and total solute flux are the same. In other studies, the fraction of the thermal component was calculated by normalizing the major ions to chloride concentration in the river and/or thermal springs with the assumption that away from the thermal area, all the Cl⁻ is derived from precipitation. Such normalization schemes are likely to underestimate the thermal Cl⁻, because significant discharge can occur directly into the river, and because thermal groundwater rich in Cl⁻ can flow laterally to great distances (e.g. Hurwitz et al., 2007a). Such normalization schemes probably also underestimate the thermal fraction of HCO₃⁻ and SO₄²⁻ which might degas from a deeper magma and the cations that result from the interaction with carbonic, sulfuric, and hydrochloric acids between a deep subsurface magma reservoir and the springs. Whereas the YPVF is located approximately 1000 km from the ocean and the precipitation contains very low Cl⁻ concentrations, significant amounts of chloride could be derived from both precipitation and magmatic sources on volcanic islands or volcanic arcs, and distinguishing the two sources is difficult.
An additional complication in the comparison of chemical weathering rate results from the dominant control of lithology. Without a clear knowledge of subsurface lithologies, separating the loads originating from weathering of silicates from those originating from the more soluble carbonates and connate water introduces significant errors (e.g., Blum et al., 1998; Gaillardet et al., 1999; Galy and France-Lanord, 1999; Jacobson et al., 2003; Meybeck, 2003). Among silicates, the weathering rate of basalt is approximately eight times greater than that of rhyolite for similar environmental conditions (Dupré et al., 2003). Additional major controls on chemical weathering rates that hinder a rigorous comparison are rainfall and air temperature (e.g., White and Blum, 1995).

Despite the above limitations some insight can be gained from comparing weathering rates in the YPVF with other regions. Whereas the total TDS flux from the Yellowstone Caldera is higher than in many studied volcanic regions, the calculated low-temperature chemical weathering rates are slightly lower than that calculated in most studies that were carried out in regions of basaltic to andesitic compositions (Table 1). For example, the TDS flux from Yellowstone Caldera (93 t/km²/year) is more than a factor of three greater than the total TDS flux from the Kamchatka River watershed (28 t/km²/year) which drains the Kamchatka Volcanic Arc, mainly of andesitic composition (Dessert et al., 2009), but the calculated low-temperature chemical weathering rate in Yellowstone (17 t/km²/year) is slightly lower than in Kamchatka (21 t/km²/year) (Table 1). In streams draining the volcanic island of Reunion, Louvat and Allègre (1997) calculated that the input from thermal springs contributes up to 68% of the TDS flux, but the overall calculated thermal fraction contribution in the volcanic island was much lower. On the volcanic island of Dominica, Lesser Antilles, Goldsmith et al. (2010) calculated

![Figure 8](image-url)
TDS fluxes slightly higher than in Yellowstone (Table 1), but did not calculate the contribution of thermal inputs. However, this study found that erosion rates in rivers draining Pleistocene aged volcanics are significantly greater than rates in rivers draining Miocene and Pliocene aged volcanics (Goldsmith et al., 2010), possibly suggesting input of thermal components.

The total TDS flux from the Yellowstone Caldera is higher than the continental world average flux of 21 to 26 t/km²/year, which includes weathering of silicates, carbonates, and evaporites (Gaillardet et al., 1999; Meybeck, 2003; West et al., 2005), but the calculated low-temperature weathering rates are slightly lower. The TDS fluxes and chemical weathering rates from Yellowstone Caldera are also much higher than TDS flux resulting from erosion rates of granitic rocks in the Clark’s Fork drainage of the Yellowstone River, which is just to the north of the YPVF (3.4 t/km²/year — Horton et al., 1999) and the calculated low-temperature chemical weathering rates in Yellowstone Caldera are comparable to the total TDS flux from the North Fork of the Shoshone River drainage, which lies entirely within the andesitic Absaroka volcanic field just east of the YPVF (18 t/km²/year — Miller and Dreyer, 1977).

6.3. Implications for chemical weathering studies in active volcanic and tectonic areas

To quantify the rates of atmospheric CO₂ consumption, some studies in volcanic regions and orogenic belts considered and quantified the yield of silicates originating from hydrothermal–rock interactions by normalizing concentrations of solutes in rivers to the concentration of Cl⁻ either in thermal springs, river water, or precipitation and other studies have assumed that thermal input is negligible. Our study highlights the significance and challenges of quantifying the relative magnitude of acid gas–hydrothermal–rock interaction and atmospheric CO₂-induced hydrolysis and the significance of the normalization scheme.

Compared with most volcanic centers, the degassing from the YPVF is extensive (Werner and Brantley, 2003; Lowenstern and Hurwitz, 2008) and thus, should be regarded as an end-member in terms of the fraction of silicate hydrolysis induced by interaction with acid gases ascending from the solid earth. However, active and passive (diffuse emissions) magmatic and/or metamorphic degassing from the solid earth occurs in all orogenic belts and active volcanoes (e.g. Kerrick and Caldeira, 1998; Kerrick, 2001; Chiordini et al., 2005; Becker et al., 2008; Evans et al., 2008; Shinohara, 2008), suggesting that silicate hydrolysis in these areas is controlled to varying degrees by hydrothermal–rock interaction with acid magmatic and/or metamorphic fluids. For example, degassing calculations from the Narayani basin of the central Himalaya suggest that the metamorphic degassing flux of CO₂ exceeds the consumption of CO₂ by chemical weathering by a factor of four (Evans et al., 2008). The possibility that in some studies the thermal component was probably underestimated is corroborated by the chemical composition of many river waters in active volcanic and metamorphic regions that are characterized by “excess Na⁺” (Hren et al., 2007), which in the case of the YPVF results from high-temperature water–rock interaction.

Given the large fraction of the thermal component in the solute flux from the YPVF and the remaining uncertainty in quantifying this fraction, we suggest that uncertainties in previously determined low-temperature chemical weathering rates and the associated atmospheric CO₂ consumption are probably much greater than reported. Greater uncertainties in chemical weathering rates in regions of active magmatism should be introduced into models of long-term CO₂-climate feedback. This could be significant, because continental basaltic lithologies account for about 30% of the total consumption of atmospheric CO₂ through weathering of continental silicate rocks (Rad et al., 2007).

7. Conclusions

- The chemical compositions of rivers that drain thermal areas in the YPVF differ significantly from the compositions of rivers that drain non-thermal areas. In the thermal areas within Yellowstone Caldera and the Norris–Mammoth Corridor a large fraction of the solutes originate from high-temperature interactions of carbonic, sulfuric, and hydrochloric acid gases ascending from depth with rhyolitic rocks. In Yellowstone Caldera the calculated hydrothermal component accounts for at least 82% of the TDS flux, 83% of the cation flux and 72% of the HCO₃⁻ flux.
- The calculated low-temperature chemical weathering rate in Yellowstone Caldera (17 t/km²/year) represents a maximum because many of the low-temperature hydrolysis reactions could be induced by CO₂ ascending from depth rather than by atmospheric CO₂. The calculated low-temperature weathering rate is slightly lower than calculated rates in other volcanic regions and comparable to the world average of large watersheds that drain also more soluble carbonates and evaporates. However, these comparisons are prone to large errors.
- There are large seasonal and inter-annual variations in river chemistry, solute discharge, and chemical weathering rates which increase with increasing water discharge. The TDS flux from Yellowstone caldera in water year 2007 (93 t/km²/year) which is lower than the calculated average for water years 2002 to 2007 (110 t/km²/year). These large variations imply that intra- and inter-annual variations are significant in calculations of chemical weathering rates and atmospheric CO₂ consumption rates.
- The TDS flux from the caldera corresponds to a denudation rate of ~1.7 cm/kyr which is comparable to the physical erosion rates. This similarity between chemical and physical erosion rates is atypical of most river systems with significant topography where physical erosion is dominant.
- Although degassing from the YPVF is extensive compared with most volcanic centers, active and passive (diffuse emissions) magmatic and/or metamorphic degassing from the solid earth followed by hydrothermal–rock interaction with acid magmatic and/or metamorphic fluids accounts for a fraction of the global silicate hydrolysis.

Acknowledgments

This study was funded by the U.S. Volcano Hazards Program. We thank Sean Eagan, Hank Heasler and Dan Mahony (Yellowstone NP) for helping with coordination and sampling and Deb Bergfeld, John Fitzpatrick, Mark Huebner, and Doug Kent (USGS) for chemical analysis. Deb Bergfeld, Art White and two anonymous reviewers are thanked for helpful and constructive comments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2010.07.001.

References

Blum, J.D., Gazis, C.A., Jacobson, A.D., Chamberlain, C.P., 1998. Carbonate versus silicate chemistry, solute discharge, and chemical weathering rates which are probably much greater than reported. Greater uncertainties in chemical weathering rates in regions of active magmatism should be introduced into models of long-term CO₂-climate feedback. This could be significant, because continental basaltic lithologies account for about 30% of the total consumption of atmospheric CO₂ through weathering of continental silicate rocks (Rad et al., 2007).


