Extensive hydrothermal rock alteration in a low pH, steam-heated environment: Hot Springs Basin, Yellowstone National Park

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ABSTRACT: We present water chemistry data for hot bubbling pools in Hot Springs Basin (HSB), one of the most thermally active basins in Yellowstone National Park, as well as chemistry and water discharge data for Shallow Creek, which drains HSB. The waters are characterized by a low pH and high sulfate and low chloride concentrations. In the bubbling pools, the molar ratios of Na/K and Mg/Ca are <1, but in Shallow Creek Na/K is >1, suggesting widespread deposition of alunite. Equilibrium calculations with SOLMINEQ88 indicate that the bubbling pools are undersaturated with respect to primary igneous minerals, supersaturated with respect to alunite, and near saturation with amorphous silica. Two of the pools are also supersaturated with kaolinite, and one is supersaturated with gibbsite and smectite. Based on the mass flux in Shallow Creek and the composition of Lava Creek tuff, we calculate a minimum erosion rate of 0.5 mm/yr in HSB, which is 1-2 orders of magnitude lower than deformation rates measured with geodetic techniques.

1 INTRODUCTION

Yellowstone National Park (YNP) (Fig. 1) hosts one of the most spectacular and vigorous hydrothermal systems on Earth (Fournier 1989). Large areas at high elevations in the eastern part of the park are underlain by vapor-dominated systems (White et al. 1971). These areas are characterized by dissolution of surficial igneous rocks from interaction with sulfuric acid (H_2SO_4) (Raymahashay 1968, White et al. 1971). Sulfuric acid is formed by the near-surface oxidation of hydrogen sulfide, which is abundant in the vapor-dominated areas (Schoen 1969).

Accurate assessment of hydrothermal alteration rates at YNP and other restless volcanoes is essential because clay-rich hydrothermally-altered rocks are weak and are prone to mechanical failure. In addition, hydrothermal alteration of rocks from interaction with extremely acidic fluids can form natural waters enriched in toxic metals (As, Hg, Se, Tl, Zn). Evaluating the hazards associated with such alteration is difficult because the degree and rate of subsurface alteration is largely unknown on any active volcano.

Previous studies on rock alteration in YNP were mainly based on the identification and classification of hydrothermally-altered minerals from research drill cores and surface deposits and the associated water compositions (Raymahashay 1968, Keith & Muffler 1978, Bargar & Beeson 1985). Most of the research holes were drilled in the liquid-dominated geyser basins of YNP, where neutral-chloride waters discharge at the surface. The alteration mineralogy and the reaction rates in these environments (Dobson et al. 2004) do not apply to vapor-dominated areas.

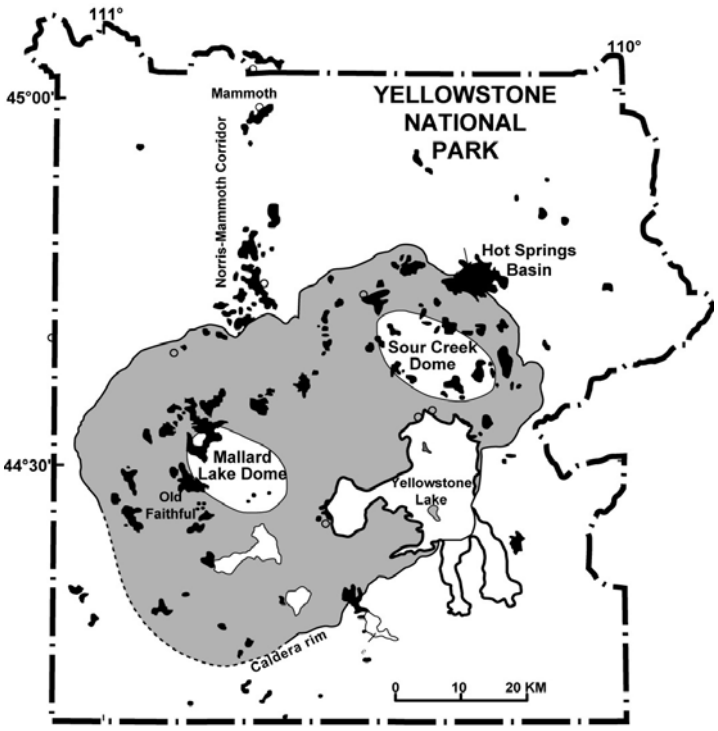
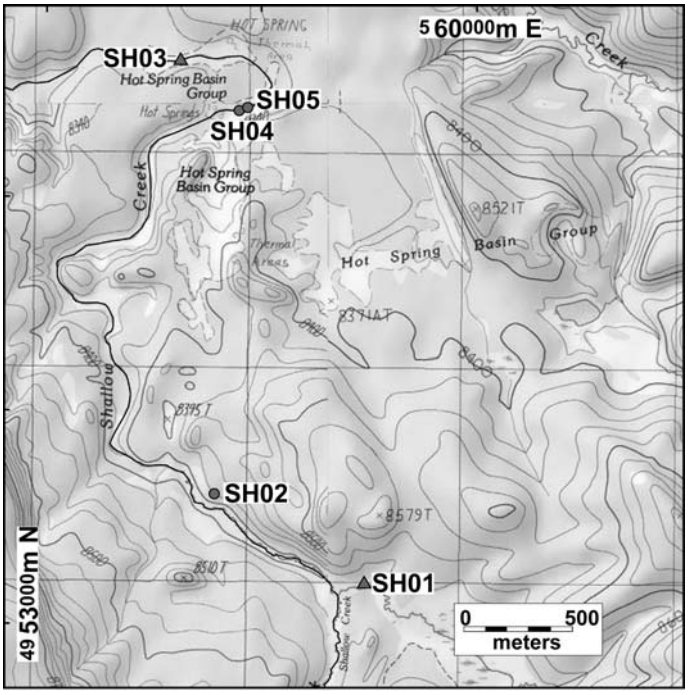


Figure 1: Map of Yellowstone National Park showing Yellowstone Caldera (shaded), thermal features (black), and location



of Hot Springs Basin (from *Christiansen* 2001).

Figure 2: Map of Hot Springs Basin showing sampling locations from Shallow Creek (triangles) and bubbling pools (circles).

The vapor-dominated zones are characterized by large diffuse soil fluxes of CO_2 (Werner & Brantley 2003), and low Cl and high SO_4 in river waters that drain these areas. A single research hole drilled in the vapor-dominated area of Mud Volcano revealed that the alteration minerals just below the ground surface consist of opal, cristobalite, kaolinite and some gypsum (Bargar & Muffler 1982).

In late summer 2006 we conducted a survey of water and gas compositions and gas fluxes in Hot Springs Basin (HSB) (Fig. 2). We present water chemistry data from the samples and use the data to infer alteration reactions and rates in one of the most thermally active basins in YNP.

2 GEOGRAPHY AND GEOLOGY OF HOT SPRINGS BASIN

HSB is located just outside the northeast boundary of the Yellowstone Caldera across from the Sour Creek resurgent dome (Fig. 1). The thermally altered ground in HSB covers an area of ~1.3 km^2 and forms local topographic depressions at an average elevation of ~2550 m. The main western depression, in which this study was conducted, covers an area of ~0.3 km^2. The basin is covered by "cemented ice-contact deposits localized by hot springs" (Christiansen 2001), showing that the basin was thermally active during the Pleistocene. HSB is surrounded by large and thick deposits of the 0.64 Ma Lava Creek Tuff, Member B, which contains 10-35% phenocrysts of quartz, sanidine (Or_{50-55}) and sodic plagioclase (An_{20}) (Christiansen 2001).

The basin hosts numerous fumaroles, mud-pots and bubbling pools that in the western depression feed into Shallow Creek, which then flows into Broad Creek, and then into the Yellowstone River. The eastern half of HSB flows into Wrong Creek, which was not sampled in this study.

3 METHODS

Samples were collected in August 2006 from Shallow Creek at locations upstream and downstream of HSB and from three bubbling pools in the basin (Table 1; Fig. 1b). At each sampling site we measured temperature and pH and collected water through a 0.45-μ filter.

All the chemical analyses were performed in the U.S. Geological Survey labs in Menlo Park, CA. SO_4, F, Cl, and Br concentrations were determined with a Dionex ICS-2000 ion chromatograph, and cation concentrations were determined with a Perkin Elmer ELAN 6000 inductively coupled plasma mass spectrometer (ICP-MS). Ammonia concentrations were determined by ion-specific electrode. Analytical uncertainties for all species are ~5%.

Water discharge was estimated by the float method (Sanders 1998) in the major tributary flowing into Shallow Creek above HSB and in Shallow Creek at the downstream end of the western depression. A correction factor of 0.85 was used to account for the effects of friction from the stream bed (Sanders 1998). The estimated error in discharge measurements is roughly ±25%. Solute flux was calculated by multiplying water discharge by solute concentration.

4 DATA

Water chemistry of the three bubbling pools and Shallow Creek upstream (SH01) and downstream

Table 1. Solute concentrations (mg/L) and molar ratios in samples from Shallow Creek and bubbling pools (bold).

	SH01	**SH02**	SH03	**SH04**	**SH05**
T (°C)	5.3	**89.2**	27.2	**87.7**	**91**
pH	7.24	**5.21**	2.45	**3.06**	**2.54**
Na	3.02	**1.6**	18.8	**130**	**30.5**
K	2.12	**3.8**	18.6	**227**	**64.1**
Ca	3.36	**0.5**	7.2	**18.5**	**4.4**
Mg	1.76	**0.15**	2.13	**4.23**	**1.72**
Fe	0.052	**<0.2**	2.9	**12.3**	**4.9**
Al	0.005	**0.19**	16.8	**2.11**	**18.2**
SiO_2	35.5	**178**	148	**288**	**282**
Cl	0.37	**0.7**	0.6	**1.7**	**0.5**

SO_4	4.29	**649**	550	**1304**	**1104**
HCO_3	24	**-**	-	**-**	**-**
F	0.28	**0.40**	0.45	**0.60**	**0.40**
NH_3	0.03	**230.6**	14.6	**165.2**	**77.2**
Mg/Ca	0.86	**0.49**	0.49	**0.38**	**0.64**
Na/K	2.42	**0.72**	1.72	**0.97**	**0.81**

(SH03) from HSB are presented in Table 1. The Alkalinity (as HCO_3) of SH01 was measured, but was assumed to be negligible in samples SH02-SH05 because of the low pH.

4.1 *Bubbling pools*

The three samples from the hot bubbling pools are characterized by very high SO_4 and low Cl concentrations, and most cation concentrations vary over an order of magnitude. The only significant cation in SH02 is NH_4^+. SiO_2 concentrations are fairly uniform, and Na/K and Mg/Ca molar ratios are <1 (Table 1).

4.2 *Shallow Creek*

The dilute waters entering HSB through Shallow Creek (SH01) have high Na/K, Mg/Ca and SiO_2/Al compared with the waters of HSB (Table 1). Shallow Creek downstream (SH03) has a lower pH, lower SiO_2/Al ratio, and higher Na/K ratio than any of the bubbling pools. Mg/Ca in SH03 is within the range of the ratio in the bubbling pools.

Water discharge and solute flux through Shallow Creek are presented in Table 2.

Table 2. Calculated water discharge (L/sec) and solute flux (kg/day) in Shallow Creek

	SH01	SH03	HSB Net
H_2O	10	65	55
Cl	0.3	2.9	2.6
SO_4	3.2	2626	2623
Na	2.2	90	88
K	1.6	89	87
Ca	2.5	34	32
Mg	1.3	10	9

The total fluxes of Cl and SO_4 from HSB account for 0.01% and 2.7%, respectively, of the Yellowstone River flux downstream at Corwin Springs (Hurwitz et al. 2007). However, these should be considered minimum values, because the fluxes for the Yellowstone River are based on annual means (for water years 2002-2004) which include periods of high flux in the spring.

5 CHEMICAL EQUILIBRIUM AND REACTIONS

The chemical data in Table 1 yields a large charge imbalance for SH03 and SH05, which is a common problem in low pH environments. To overcome this, water compositions were speciated and charge-balanced by varying the pH using the geochemical code SOLMINEQ88 (Kharaka et al. 1988). Modeled results indicate that the bubbling pools are supersaturated with respect to several alteration minerals (Table 3).

The waters are all undersaturated with gypsum and anhydrite and are at or near saturation with amorphous silica. All of the bubbling pools are supersaturated with alunite ($KAl_3(SO_4)_2(OH)_6$). Sample SH02 is also supersaturated with kaolinite ($Al_2Si_2O_5(OH)_4$) and the various smectites. Due to the low pH and relatively low temperature, the downstream sample from Shallow Creek (SH03) is undersaturated with alunite, kaolinite and smectite, but is slightly supersaturated with amorphous silica.

The chemical equilibrium calculations suggest that thermal waters in HSB are undersaturated with the primary igneous minerals in the Lava Creek tuff and therefore, these minerals are expected to dissolve. An exception is sample SH02, which is slightly saturated with sanidine.

Table 3. Calculated values of pH and log (Q/K) for various minerals using SOLMINEQ88

	SH02	SH03	SH04	SH05
pH	5.21	2.30	3.06	2.32
Albite	-1	-8.19	-3.52	-5.54
Sanidine	0.12	-7.13	-2.54	-4.53
Silica	-0.24	0.08	-0.02	-0.05
Alunite	3.42	-3.76	3.06	2.05
Kaolinite	5.88	-5.44	0.49	-0.82
Gibbsite	0.49	-4.57	-2.42	-3.06
Smectites	4.92 to 5.64	-8.97 to -8.57	-1.15 to -0.81	-3.13 to -2.65

Compared to the bulk chemistry of Lava Creek Tuff, Member B (Christiansen 2001), the waters are enriched in Na and Ca and depleted in SiO_2. This suggests preferential dissolution of sodic plagioclase and/or deposition of SiO_2. The higher Na/K in the water compared with the tuff could also reflect control by alunite. There is also some loss of Al – probably to kaolinite - to make up for the increased dissolution of plagioclase.

The rate of sulfuric acid formation in HSB can be calculated by dividing the SO_4 flux (~2,600 kg/day) by the area of HSB above the sampling site SH03 (0.3 km^2). The calculated SO_4 flux (9 $g \cdot m^{-2} \cdot day^{-1}$) is similar to the fluxes measured in many areas of acid-altered ground in the Norris-Mammoth corridor (Fig. 1), just to the north of the Yellowstone Caldera (Schoen 1969).

6 EROSION RATES

To obtain an estimate of chemical erosion rates we calculate the mass of rock that must dissolve to account for the solute loads at Shallow Creek (Table 2). Most of the chemical erosion occurs in the shallow sub-surface forming dissolution voids. However, with time, the altered and weak roof of these voids collapse and thus, the ground surface is lowered. We assume that NH_4 and SO_4 are derived from upflowing gases, whereas other cations, anions, and Si (as SiO_3) are derived from leaching of the rock. The net load originating from HSB is calculated by subtracting solute fluxes entering HSB (SH01) from the flux downstream from HSB (SH03).

Following the above assumptions, 955 kg of minerals are dissolved daily to account for the load in Shallow Creek. Taking into account the density of upper part of Lava Creek Tuff, Member B (2,300 kg/m^3) (Christiansen 2001) and an area of 0.3 km^2, this amounts to an erosion rate of 0.5 mm/year. This rate is 1-2 orders of magnitude less than current deformation rates as measured with geodetic techniques (Lowenstern et al. 2006). The average depth of the depression relative to surrounding ground is ~10 m, which could suggest that the chemical erosion rate has remained roughly constant since the end of glaciation. However, the calculated fluxes and erosion rates are minimum estimates because solute fluxes in YNP rivers are dominated by seasonal effects with peak fluxes following snowmelt in April-June (Hurwitz et al. 2007). Thus, the value we calculated based on fluxes in late August might not be accurate for the annual mean if snowmelt greatly increases the mobilization of solutes into Shallow Creek. Deposition of alteration minerals during dry periods, followed by dissolution and flushing of these materials during heavy recharge events is a logical possibility that we cannot evaluate with present data.

7 CONCLUSIONS

The water chemistry data from HSB presented in this paper sheds new light on the alteration rates in the vapor-dominated zones of YNP. We infer the following:

1. The waters are characterized by low pH, high sulfate, and low chloride concentrations.
2. The thermal waters are undersaturated with respect to primary igneous minerals, which can dissolve into solution, whereas alunite, kaolinite, gibbsite and smectite can be precipitated. Equilibrium calculations also suggest that the thermal waters are near saturation with amorphous silica.
3. Based on the mass flux in Shallow Creek, we calculate a minimum erosion rate of 0.5 mm/yr in HSB, which is 1-2 orders of magnitude less than deformation rates measured with geodetic techniques.
4. The high erosion rates and the transformation of igneous rocks to mechanically weak clays in areas overlying YNP's vapor-dominated systems poses a hazard for hikers and any future road and building construction.

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