Carbon dioxide and hydrogen sulfide degassing and cryptic thermal input to Brimstone Basin, Yellowstone National Park, Wyoming

D. Bergfeld a,⁎, W.C. Evans b, J.B. Lowenstern a, S. Hurwitz b

a Volcano Science Center, U.S. Geological Survey, MS 910, Menlo Park, CA 94025, USA
b National Research Program, U.S. Geological Survey, MS 434, Menlo Park, CA 94025, USA

A R T I C L E   I N F O

Article history:
Received 22 March 2012
Received in revised form 13 August 2012
Accepted 1 September 2012
Available online 7 September 2012

Editor: D.B. Dingwell

Keywords:
CO₂ flux
Acid-sulfate δ¹³C-shift
Cold-degassing

A B S T R A C T

Brimstone Basin, a remote area of intense hydrothermal alteration a few km east of the Yellowstone Caldera, is rarely studied and has long been considered to be a cold remnant of an ancient hydrothermal system. A field campaign in 2008 confirmed that gas emissions from the few small vents were cold and that soil temperatures in the altered area were at background levels. Geochemical and isotopic evidence from gas samples (³He/⁴He−3R α, δ¹³C-CO₂−3‰) however, indicate continuing magmatic gas input to the system. Accumulation chamber measurements revealed a surprisingly large diffuse flux of CO₂ (~277 t d⁻¹) and H₂S (0.6 t d⁻¹). The flux of CO₂ reduces the ⁸⁷O content of the overlying cold groundwater and related stream waters relative to normal meteoric waters. Simple isotopic modeling reveals that the CO₂ likely originates from geothermal water at a temperature of 93±19 °C. These results and the presence of thermogenic hydrocarbons (C₁:C₂~100 and δ¹³C-CO₂~46.4 to −42.8‰) in gases require some heat source at depth and refute the assumption that this is a "fossil" hydrothermal system.

1. Introduction

The hydrothermal system at Yellowstone discharges abundant carbon dioxide (CO₂) both from point-sources such as roiling pools and fumaroles, and diffusely through the soil. The first studies to quantify the diffuse CO₂ emissions at Yellowstone (Werner et al., 2000; Werner and Brantley, 2003) found that the largest emissions occurred in the acid-sulfate areas, which are concentrated in the east part of the caldera (Fournier, 1989). Based on efflux measurements at several acid-sulfate areas, Werner and Brantley (2003) estimated that diffuse CO₂ emissions at Yellowstone total ~45±16 kilotonnes per day (kt d⁻¹). That study provided the motivation to measure gas efflux at additional areas in the park in order to better constrain total emissions. Subsequent studies of diffuse gas emissions at Yellowstone include acid-sulfate areas around Hot Spring Basin (Werner et al., 2008) and areas with neutral chloride and carbonate-rich waters (Lowenstern et al., 2012). These recent studies have also included measurements of H₂S efflux.

Brimstone Basin is an acid-sulfate area located in a remote part of the park near the Southeast Arm of Yellowstone Lake (Fig. 1). The area is characterized by highly-altered ground, typical of other acid-sulfate regions at Yellowstone, but lacks other characteristic features of acid-sulfate terrains such as fumaroles and mudpots, and importantly, shows no discernable thermal anomaly. Ever since the earliest reports from visitors to the area, it has been considered a "fossil" system (Langford, 1905). However, our 2008 field campaign detected and quantified substantial CO₂ and H₂S emissions from portions of Brimstone Basin that are comparable in magnitude to those in hot acid-sulfate areas. In addition, we found three locations with focused gas emissions and use chemical and isotope results from samples of gas and waters at those sites to evaluate subsurface temperatures. We present here the first comprehensive study of diffuse gas emissions from a large, non-thermal degassing area at Yellowstone and help to constrain the role that cold gas emissions might play in the overall gas discharge at Yellowstone.

2. Field site description

Brimstone Basin is characterized by large expanses, ~1.1 km² in total, of highly-altered Tertiary-aged andesite of the Langford formation of the Absaroka Volcanic Supergroup rocks (Christiansen, 2001). The altered areas are mostly devoid of vegetation and the barren surface is generally bright white in color and is recognizable from afar. The alteration at Brimstone Basin is contiguous with a series of NNW trending faults (Richmond and Pierce, 1972; Fig. 2) with discrete altered areas separated from one another by Lodgepole Pine forest. Dates for the alteration have not been determined, but cemented ice-contact deposits indicate temperatures were hot enough to melt ice, and suggest that there was hydrothermal activity during the Pleistocene (Robert L. Christiansen, personal communication, 11/16/2010). The presence of sulfur and sulfur-bearing minerals is evident across the altered areas at Brimstone Basin, and there is a great deal of physical evidence of present-day degassing of H₂S. Some areas are covered by friable gray-to-black colored sulfur flows that are
believed to have formed when elemental sulfur deposits were ignited during a forest fire (Hutchinson, 1987). Other areas have conspicuous mounds of buff-to-gray colored rocks that are often coated with sublimates of sulfur-bearing minerals. The strong acrid odor of H2S is evident around the mounds. We also identified several locations where gas was bubbling through the shallow water of Alluvium Creek, a cold acidic stream that drains part of Brimstone Basin (Fig. 3). Two of the degassing locations had a vigorous gas efflux causing the water to roil several centimeters above the surface. Photos of field site are included in the appendix.

Previous research at Brimstone Basin has focused on detailed geochemical studies of the water in Alluvium and Columbine Creeks, the two main creeks that drain Brimstone Basin (Ball et al., 2001, 2002; McCleskey et al., 2005; Nordstrom et al., 2009). The pH of the creek waters reflects the association with gas upflow. Alluvium Creek waters are acidic with reported pH values around 2.5 and as low as 1.23 (Nordstrom et al., 2009). Reported pH values for Columbine Creek waters and its tributaries range from 2.01 to 7.07 (Ball et al., 2001; Gemery-Hill et al., 2007). Within the study area, Alluvium Creek and a tributary to Columbine Creek flow from the east through part of the degassing ground toward their respective discharge points at Yellowstone Lake (Fig. 3). The discharge from Alluvium Creek is variable along its length, and during the 2008 study the lower reach of the creek was dry – 1 km downstream from Brimstone Basin.

3. Methods

3.1. Flux and temperature measurements

CO2 and H2S flux measurements were made across two of the largest areas of alteration on September 24 and 25, 2008. The flux grids were irregularly-shaped with boundaries set by the edges of the altered
Fig. 2. Rectified orthophoto of the Brimstone Basin area overlain with the polygon from the Yellowstone National Park map of thermal areas (in gray), our boundaries for altered/thermal ground (in pink) and the locations of diffuse gas measurements in the west and east grids (red dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) Faults (ball on downthrown side) from Richmond and Pierce (1972).

Fig. 3. Topographic map showing sample locations from this and other studies as circles and triangles and flux grids in gray. Circles show locations of samples collected from Alluvium Creek and triangles show locations of samples collected from Columbine Creek. Pink circles show Alluvium Creek samples with oxygen isotope values that are shifted >1.5‰ relative to the global meteoric water line. Note that the base map incorrectly lists the gas upflow zones as “thermal areas”. Published stable isotope values are from Ball et al. (2001, 2002), Bergfeld et al. (2011), Gemery-Hill et al. (2007), McCleskey et al. (2005).
ground. Spacing between individual measurement sites was around 15 to 20 m. Air temperature was recorded intermittently in the shade on both days. On September 24th, soil temperatures at 10 cm were recorded at 36 sites between 10:00 and 13:40.

Gas fluxes were determined using two West Systems® instruments (Chiodini et al. 1996; 1998), one capable of measuring fluxes of CO₂ and H₂S in tandem, and a second instrument that measured only CO₂. Most of the flux measurements were made over bare ground with two teams working along parallel traverses. Toward the end of the second day the battery in instrument #1 failed, and from then on, only CO₂ fluxes were determined. A total of 284 CO₂ flux measurements were attempted at 144 sites in the east grid and 140 sites in the west grid (Table 1). We completed a total of 120 H₂S flux measurements including 49 in the east grid and 71 in the west grid. We obtained better coverage of the altered zone in the western area.

Both flux instruments were equipped with LI-COR® 820 infrared CO₂ analyzers that were field-calibrated from 0 to 2000 ppm CO₂. The H₂S concentrations were determined on instrument #1 using a Dräger Polytron® II electrochemical cell capable of measuring H₂S concentrations up to 25 ppm. Calibration of the H₂S sensor was performed by the manufacturer. We used a 2.7-L cylindrical accumulation chamber (~0.314 m² base x ~0.097 m height) with instrument #1, since the small chamber provided the best opportunity to quantify the H₂S flux. Graphical analysis of the H₂S flux data indicated that the minimum quantifiable H₂S flux was 0.1 g m⁻² d⁻¹. For instrument #2 we used either the 2.7-L or a cylindrical 6-L (~0.314 m² base x ~0.198 m height) accumulation chamber, depending on the rate of CO₂ discharge. By using different-sized chambers we were able to maximize our CO₂ measurement capability at areas with very high fluxes while keeping the analyzer configured for maximum precision. Detailed explanations concerning flux measurement techniques are presented in Lewicki et al. (2005) and Bergfeld et al. (2006).

### 3.2. Gas flux and CO₂ emission calculations

The flux was calculated for each measurement site using the rate of gas discharge, the area of the footprint incorporated by the accumulation chamber, the volume of the measurement system, the barometric pressure and air temperature during the measurement, and the ideal gas law (Welles et al., 2001). The flux is reported in units of grams of gas (CO₂ or H₂S) per square meter per day (g m⁻² d⁻¹).

To estimate the total diffuse CO₂ emissions from Brimstone Basin, the average CO₂ flux for each grid was calculated from results of sequential Gaussian simulations (sGs) of the measured flux. The simulations were performed using the sgsim module of the GSLIB program (Deutsch and Journel, 1998) following methods outlined in Cardellini et al. (2003) and Lewicki et al. (2005). The simulations produce multiple equiprobable outcomes of the spatial distribution of the flux over a 5 m² grid cell. The mean CO₂ flux was determined from the summation of 1000 simulations and differences in the simulations gave the upper and lower bounds on the estimate. The total diffuse CO₂ emissions for the two flux grids were calculated using the sGs-determined mean flux values multiplied by the grid areas. Total emissions are reported in units of metric tonnes of CO₂ per day (t d⁻¹).

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<th>Avg. flux g m⁻² d⁻¹</th>
<th>Discharge t d⁻¹</th>
<th>/−/ t d⁻¹</th>
<th>Number of Measurements</th>
<th>Number of Quantifiable flux</th>
<th>Max. flux g m⁻² d⁻¹</th>
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### Table 1

Summary statistics for gas flux measurements.

Fig. 4. Histograms of the CO₂ flux data for A) east grid (n = 144) and B) west grid (n = 140). Units in g m⁻² d⁻¹ for all measured sample locations. The flux data are positively skewed, and the west grid has more sites with a high CO₂ flux.

Fig. 4. Histograms of the CO₂ flux data for A) east grid (n = 144) and B) west grid (n = 140). Units in g m⁻² d⁻¹ for all measured sample locations. The flux data are positively skewed, and the west grid has more sites with a high CO₂ flux.
3.3. Sample collection and analysis

Samples of gas and water were collected at three locations along Alluvium creek (Fig. 3). At all of the sites the gas bubbled up through water and was collected using a funnel and Tygon® tubing connected to an evacuated doubleport bottle containing 4-normal sodium hydroxide (NaOH). At two of the sites a second sample of gas was collected into copper tubing for determination of helium isotope values. The pH of water and was collected brim-full in glass bottles.

Gas and water chemistry were determined at the USGS in Menlo Park, California. Helium isotopes were determined at the USGS in Denver, Colorado. Isotope ratios (δD and δ18O) for collected waters and carbon isotope ratios (δ13C) of methane (CH4) in the headspace gas and CO2 exsolved from the NaOH solution were determined at the USGS Reston Stable Isotope Laboratory in Virginia. Details on sample preparation and analytical uncertainties are presented in Bergfeld et al. (2011).

3.4. Calculation of altered terrain at Brimstone Basin

The existing GIS coverage of thermal ground for Yellowstone National Park showed 2.48 km² of “thermal area” at Brimstone Basin (Yellowstone Center for Resources, unpublished data 2003). However, the coverage included several large expanses of forest and stream valleys blanketed with mobilized altered materials, and we consider it an overestimate of actual altered ground. We re-estimated the area (1.1 km²) by drawing polygons around bare regions on the relevant orthophoto quadrangles (shown in Fig. 2), hypothesizing that such areas experience a steady flow of acid gas through the soil, thereby resulting in little vegetation. Field observations validated that the barren areas consisted of acid-altered ground.

4. Results

4.1. CO2 and H2S Fluxes

The size of each grid and the range of measured CO2 fluxes within each grid were similar (Table 1). Each grid had several sites with CO2 fluxes below the detection limit of the instruments (n = 5) with maximum fluxes around 2950 and 3000 g m⁻² d⁻¹ in the west and east grids, respectively (Figs. 4A and 4B). The west grid had considerably more sites with CO2 fluxes >500 g m⁻² d⁻¹, and it follows that the average CO2 flux for the west grid at about ~300 g m⁻² d⁻¹, was higher than the average for the east grid ~190 g m⁻² d⁻¹ (Table 1). Emission estimates derived from the sGs simulations of the CO2 flux indicate that the total diffuse CO2 emissions from the studied area
was about 90 t d$^{-1}$ with over half (55 t d$^{-1}$) discharged from the west grid (Table 1).

The contour plots of the CO$_2$ fluxes from the sGs simulations highlight the differences in the pattern of CO$_2$ emissions across the two grids (Fig. 5). Overall the west grid was characterized by high CO$_2$ fluxes with only a few localized low-flux areas that mostly occurred along the margins. By comparison, the east grid had more areas that were characterized by low-to-moderate fluxes, and the sites with high fluxes were separated by an east-west trending area of low emissions. A few additional high flux sites were clustered in the southern part of the east grid.

We made 120 measurements to determine the H$_2$S flux and found 19 sites, including 13 in the west grid and 6 in the east grid, that had flux values between 0.1 and 25 g m$^{-2}$ d$^{-1}$ (Table 1). In the west grid the H$_2$S emissions were mainly concentrated in the center of the grid as compared to the east grid, where sites having a detectable H$_2$S flux were scattered. At both grids there were additional sites where we recorded rising H$_2$S concentrations in the accumulation chamber, but when the rate data did not produce an acceptable linear trend we assigned a zero (below detect) value. The average H$_2$S record was 0.54 g m$^{-2}$ d$^{-1}$, though when the rate data did not produce an acceptable linear trend we assigned a zero (below detect) value. The average H$_2$S record was 0.54 g m$^{-2}$ d$^{-1}$. It is important to note that we only made H$_2$S measurements at about half of the sites in the west grid and at a third of the sites in the east grid. Given this limited dataset we feel detailed comparison of H$_2$S fluxes across the two grids is not warranted.

A scatter plot of the CO$_2$ and H$_2$S fluxes from all measured sites shows the fluxes were positively correlated. Quantifiable H$_2$S fluxes only occurred at sites where the CO$_2$ flux was >400 g m$^{-2}$ d$^{-1}$ but there were some sites with high CO$_2$ fluxes that did not have a flux of H$_2$S (Fig. 6). Polynomial regression of the data pairs shows that overall the two components of the gas flux are well correlated, with an $R^2$ value of 0.94 (Fig. 6). The regression line is controlled by the data pair with the highest CO$_2$ and H$_2$S values but even after removing that pair there is a good correlation ($R^2=0.82$). We can exploit the gas flux relations and use the CO$_2$ flux values from sites where we did not measure H$_2$S to predict what sites may have had a diffuse discharge of H$_2$S. These calculations indicate that 9 additional sites in the west grid and 4 sites in the east grid may have had H$_2$S fluxes between 0.1 and 10.4 g m$^{-2}$ d$^{-1}$ and 0.1 and 2.4 g m$^{-2}$ d$^{-1}$, respectively (Fig. 5).

### 4.2. Soil and air temperatures

Comparison of the soil and air temperatures on September 24th generally shows increasing temperatures over the course of the day (Fig. 7a). Soil temperatures at a depth of 10 cm over a ~3 h interval were between 2.1 and 8.3 °C, and were substantially lower than ambient air temperatures during the same time interval. This contrasts greatly from shallow soil temperatures in areas of steaming ground, where the heat from steam condensation obscures diurnal effects caused by solar heating (Bergfeld et al., 2006). At Brimstone Basin, the average 10-cm soil temperature was 4.2 °C at 36 sites (Fig. 7). The absence of steaming ground, which is typically associated with active hydrothermal systems, is consistent with minimal shallow heat input to Brimstone Basin. Thermal IR (ASTER and MODIS) satellite data also fail to reveal any discernible geothermal heat output from this area (Vaughan et al., 2012).

### 4.3. Gas and water chemistry

Apart from H$_2$ and air components, the three gas samples had nearly identical compositions including bulk chemistry of the gas, $\delta^{13}$C values of CO$_2$, and R/$R_{\alpha}$ values of helium isotopes (Table 2). CO$_2$ is the main component of the dry gas followed by H$_2$S, N$_2$, CH$_4$, and He with lesser amounts of Ar, H$_2$, O$_2$ and C$_2$-C$_3$ hydrocarbons (Table 2). Nitrogen to argon ratios are around 30-35, much lower than ratios found in air, and are more representative of dissolved gas in air-saturated meteoric water. The $\delta^{13}$C values of CO$_2$ were $-3.0$ and $-2.9\%$ and $R_{\alpha}/R_{\beta}$ values were 2.99 and 3.03. The $\delta^{13}$C-CH$_4$ values of gas from the 2 west grid locations were similar ($-43.3$ and $-42.8\%$) and CH$_4$ from the east grid was $-46.4\%$, about $3\%$ lower (Table 2). These $\delta^{13}$C-CH$_4$ values and the CH$_4$/C$_2$H$_6$ ratios are typical of thermogenic gases as have been described in the eastern part of Yellowstone National Park (Lorenson and Kvenvolden, 1993).

The applicability of gas geothermometers to cold gas emissions is not well studied. Nevertheless, we calculated “reservoir” temperatures using four common gas geothermometers and obtained variable results, ranging from 87 to 279 °C (Table 2). The temperatures estimated for the 3 sites when using any single geothermometer are for the most part comparable except for T$_{CO2}$, which may be influenced by loss of H$_2$ in the near surface as described by Chiodini (1994). The highest temperature estimates come from hydrocarbon-based geothermometers, which are slow to equilibrate and slow to reset (Darling, 1998; Tassi et al., 2007). As discussed by Darling (1998), hydrocarbon ratios can provide a reasonable estimate of subsurface temperature even if the hydrocarbons reflect thermogenic breakdown of buried organic material rather than true chemical equilibrium.

The composition of the three water samples were variable, reflecting in-part their respective locations along Alluvium Creek (Table 3, Fig. 3). All samples were collected at actively degassing sites. The waters are classified as acid–sulfate with pH values below 5, and having high SO$_4$ and low Cl concentrations, respectively (White, 1957). The low Cl concentrations rule out any input of thermal water from depth. Sample 18, collected from a vigorously bubbling pool of standing water adjacent to Alluvium Creek had 2200 mg L$^{-1}$ SO$_4$ and was more concentrated than the other sites. Samples 19 and 20 were flowing water in Alluvium Creek, albeit from different parts of the reach (Fig. 3). Sample 20 had 2000 mg L$^{-1}$ SO$_4$ similar to sample 18, while sample 19 from upper Alluvium Creek had only 1100 mg L$^{-1}$ SO$_4$ (Table 3).

The stable isotope composition of 2 samples of flowing water collected from Alluvium Creek were similar, while that of sample 18 from the pool had lower $\delta^{13}O$ and $\delta^{18}O$ values, the opposite of what would be expected from evaporation (Table 3; Fig. 8a). All of the water samples were collected where gas was discharging and all are unusual in that they plot to the left of the global meteoric water line (GMWL) of Craig (1961). Comparison of our results with data from the previous water-chemistry studies at Brimstone Basin (Ball et al., 2001, 2002; McCleskey et al. 2005; Gemery-Hill et al., 2007)

### Table 2

Analytical results of gases collected at Brimstone Basin, Yellowstone National Park, WY (see Bergfeld et al., 2011 for discussion of analytical uncertainties). Values in volume percent except as noted. X$_g$ = mol fraction of gas, bdl = below detection, R/$R_{\alpha}$ = $^{3}He$/He ratio in the sample relative to that in air, R/$R_{\alpha}$ is corrected for atmospheric components in the sample. Gas geothermometers are from the following: T$_{CO2}$ from D’Amore and Panichi, 1980, T$_{CO2}$,CH$_4$ from Giggenbach, 1996, T$_{CO2}$,C$_2$ from Girgenti et al., 1982, T$_{CO2}$,C$_2$ from Tassi et al., 2001, 2002; McCleskey et al. 2005; Gemery-Hill et al., 2007)

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<th>NH$_3$</th>
<th>He</th>
<th>$\alpha$</th>
<th>$\beta$</th>
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show that many waters from Brimstone Basin plot to the left of the GMWL (Fig. 8a). This “negative” isotopic shift distinguishes Brimstone Basin waters from other cold waters at Yellowstone.

5. Discussion

5.1. Gas discharge from Brimstone Basin

The study area covered approximately one third of the altered ground at Brimstone Basin (Table 1) and we use the measured fluxes to estimate total diffuse CO₂ emissions from the entire area. By assuming the unknown area has emissions similar to the average flux from the east grid (187 g m⁻² d⁻¹) and summing with the measured grid results, our estimate for total diffuse CO₂ emissions for all of Brimstone Basin is 230 ± 80 t d⁻¹ (Table 1). If instead we assume emissions from the unstudied ground are similar to the average flux from both grids ~250 g m⁻² d⁻¹, then total diffuse CO₂ emissions would be around 277 ± 97 t d⁻¹.

We determined an estimate of the amount of diffuse H₂S discharge by using a similar extrapolation of the mean H₂S flux (0.54 g m⁻² d⁻¹) from the measured sites over the footprint of both grids. Using the data from the two grids we estimate H₂S emissions at ~0.2 t d⁻¹ for the studied ground and ~0.6 t d⁻¹ for all of Brimstone Basin. These are likely minimum estimates as we identified sites with a H₂S flux that were too low for our instrument to detect, and as described above the CO₂ flux data predict that additional sites should have diffuse H₂S emissions.

At 3 sites with high CO₂ fluxes >1100 g m⁻² d⁻¹ the mass flux ratios of H₂S:CO₂ are similar to H₂S:CO₂ mass ratios in the gas samples (0.0050; Table 2; Fig 6). At most of the sites the H₂S:CO₂ mass ratio was much lower than in the gas samples. The difference likely reflects H₂S loss from scrubbing by groundwater as well as formation of sulfur-bearing mineral encrustations. Comparison of the H₂S:CO₂ mass ratio in the diffuse discharge (0.0022 from Table 1) with the mass ratio of H₂S:CO₂ in the gas samples (0.0050; from Table 2) indicates that the diffuse discharge has lost about 57% of its H₂S due to scrubbing. This is a minimum estimate of H₂S scrubbing because the gas samples were collected through cold water and that gas may have already lost H₂S.

5.2. CO₂ emissions at Brimstone Basin compared with thermal acid sulfate areas

A similar study of diffuse CO₂ emissions at Hot Spring Basin, one of the largest areas of thermal acid sulfate ground at Yellowstone (Fig. 1), found that the average diffuse CO₂ flux was 320 g m⁻² d⁻¹ (Werner et al., 2008), similar to the 300 g m⁻² d⁻¹, reported here for the west grid at Brimstone Basin. Thus, surface temperature is not necessarily a reliable gauge of CO₂ flux at Yellowstone.

The average CO₂ fluxes for both areas are lower than the ~1200 g m⁻² d⁻¹ proposed by Werner and Brantley (2003) for all acid sulfate areas at Yellowstone. Their estimate, from early studies of diffuse degassing at Yellowstone, is heavily weighted on measurements from the Mud Volcano area, where the fumaroles and fying pans have the highest gas/steam ratios of any in Yellowstone (Bergfeld et al., 2011). Mud Volcano thermal features also discharge gas with the highest gas/steam ratios of any in Yellowstone (Bergfeld et al., 2011). Mud Volcano thermal features also discharge gas with the highest gas/steam ratios of any in Yellowstone (Bergfeld et al., 2011).

5.3. Brimstone Basin gas and evidence for a heat source

The composition of the gas from Brimstone Basin distinguishes it from gas from most other acid sulfate areas at Yellowstone. The gas is low in atmospheric components such as N₂, Ar and O₂ (Table 2), is relatively low in CH₄, and has relatively high concentrations of He (Fig. 9a). On a N₂–He–Ar diagram (Fig. 9a) for gas from Brimstone Basin and ~0.6 t d⁻¹ from other acid sulfate areas at Yellowstone. The Brimstone Basin gases are comparatively enriched in CO₂ relative to H₂S (Fig. 9b).

The lack of Cl in Brimstone Basin waters precludes any direct input of thermal water; therefore only gas-phase indicators can be used to assess subsurface temperatures. Although the gas discharge at Brimstone Basin is cold, several lines of evidence from gas chemistry indicate a connection to a hot system at depth. The δ¹³C–CO₂ values are −2.9‰ and −3.0‰ are typical of CO₂ in Yellowstone high-temperature gas, which ranges between −5.0 and +0.4‰ with an average of −3.3 ± 0.9‰ (from data of Bergfeld et al., 2011). The helium isotope ratio of 3.0 Ra for Brimstone Basin gas clearly indicates that some of the helium is from a magmatic source. Even though this value is lower than ratios in gas from thermal acid sulfate areas such as Mud Volcano (−16 Ra) or Hot Spring Basin (4.7–6.7 Ra), it is slightly greater than the ratio (1.1–2.9 Ra) in gas emissions from a 205 °C reservoir at Heart Lake Geyser Basin at the southern edge of the Yellowstone caldera (Kennedy et al., 1985; Werner et al., 2008; Bergfeld et al., 2011; Lowenstern et al., 2012).

Relations between C3H₈ and CH₄ concentrations and δ¹³C–CH₄ values reveal the gases have a distinct thermogenic signature and do not originate primarily from shallow microbial activity, which would result in higher CH₄/C3H₈ and lower δ¹³C–CH₄ (Fig. 10, after Pohlman et al., 2009). Similarly, equilibrium temperatures calculated from several gas geothermometers indicate temperatures in excess of 200 °C (Table 2). The range of temperatures calculated from various gas geothermometers likely reflects the variable rates at which gas components re-equilibrate as well as changes in gas contents between the reservoir and the discharge point. As noted earlier, near surface loss of H₂ lowers temperature estimates using T₂P. Thermal equilibration for hydrocarbon-based geothermometers is slow (Darling, 1998; Tassi et al., 2007), and these geothermometers are relatively insensitive to processes that cause cooling of reservoir temperatures, such as dilution by cold groundwater and these geothermometers may be the most reliable in this setting.

5.4. δ¹⁸O shift in Brimstone Basin water

The isotopic composition of Alluvium Creek waters that flow through the active degassing areas are shifted off the global meteoric water line to lighter δ¹⁸O values without an apparent shift in δD.
Previous studies at Brimstone Basin have shown that δ¹⁸O values of waters in Columbine Creek and in Alluvium Creek above the area of active degassing are not shifted and are indistinguishable from other cold waters at Yellowstone (Fig. 3) (Ball et al., 2001, 2002; Gemery-Hill et al., 2007; Nordstrom et al., 2009). In addition, by the time Alluvium Creek discharges into Yellowstone Lake, dilution by unaffected ground water eliminates the δ¹⁸O shift.

Waters that exhibit negative shifts in δ¹⁸O compositions with only small changes in δD are somewhat unusual in hydrothermal systems, as isotopic exchange related to processes such as boiling, evaporation, or water-rock interaction will increase ¹⁸O contents in the residual water such that they plot to the right of the GMWL (Criss and Taylor, 1986). Taran et al. (1998) attributed a negative oxygen shift of up to 3‰ in waters at El Chichón volcano to hydration of fresh pumice. Such a process is not applicable to Brimstone Basin waters where the rocks are heavily altered and the oxygen shift exceeds 5‰ in some waters. Instead we...
invoke a process proposed for oxygen-shifted waters in other areas with high CO₂ degassing (Pauwels et al., 1997; Fritz and Frape, 1982; Vuataz and Goff, 1986; Matthews et al., 1987; Cartwright et al., 2002). The negative oxygen shift reflects absorption of CO₂ gas rising from deep thermal water into shallow, cold groundwater. Near-surface isotopic equilibration then occurs at ambient temperatures, with subsequent loss of CO₂ to the atmosphere. This process simultaneously enriches the CO₂ gas and depletes the water in 18O because the isotope fractionation between CO₂ and H₂O increases greatly as equilibration temperatures decline (Friedman and O’Neil, 1977, and references therein). Two conditions must be met: 1) the rate of CO₂ gas discharge must be large enough in relation to the throughput of shallow groundwater that the isotopic composition of the CO₂ can affect the O-isotope mass balance; 2) the deep thermal water must be warmer than surface waters, but not too warm, or accompanying steam would result in significant surface heating, which is not seen at Brimstone Basin.

We used the diffuse CO₂ discharge calculated for Brimstone Basin (277 t d⁻¹ − 6.3 Mmol d⁻¹) to assess whether condition 1 might be met, though there remain three unknowns: the total throughput of shallow groundwater, the temperature of the deep thermal water, and its δ¹⁸O value. We chose sample #20 from Alluvium Creek (Fig. 3) to represent the average oxygen-shifted water −3.5% to the left of the GMWL (Fig. 8). At an average summertime surface water temperature of −14 °C (Ball et al., 2001, 2002; McCleskey et al., 2005; Nordstrom et al., 2009; Bergfeld et al. 2011), the δ¹⁸O value of CO₂ in equilibrium with this water is +20.2% (Friedman and O’Neil, 1977, and references therein). The through put of shallow groundwater and the temperature difference between the deep thermal and shallow groundwaters are related through mass balance such that:

\[
\left( F_w, \delta^{18}O_{w_i} \right) + \left( 2.F_g, \delta^{18}O_{g_i} \right) = \left( F_w, \delta^{18}O_{w_f} \right) + \left( 2.F_g, \delta^{18}O_{g_f} \right)
\]

which reduces to:

\[
F_w, \Delta \delta^{18}O_{w_f-w_i} = 2.F_g, \Delta \delta^{18}O_{g_f-g_i}
\]

where Fw is the throughput of shallow groundwater, and Fg is the measured diffuse discharge of CO₂ (both in Mmol d⁻¹). Δδ¹⁸Ow_f-w_i is the difference between the initial and final oxygen isotopic ratios of the shallow groundwater, and Δδ¹⁸Og_f-g_i is the temperature-dependent difference between the final and initial oxygen isotopic ratios of CO₂ in equilibrium with the shallow groundwater and deep thermal water, respectively. The factor of 2 accounts for the two oxygen atoms in each molecule of CO₂.

For the initial test we assigned a δ¹⁸O-H₂O value of −18.4‰ to the deep thermal water (δ¹⁸Ow_f), based on an estimated δO value of −149‰ (Truesdell et al., 1977) and the regression line through the Yellowstone hot waters in Fig. 8a. To satisfy condition 2, our calculations assume a thermal water temperature of 90 °C, just below the local boiling temperature. Under these constraints Fw is 30.5 Mmol d⁻¹, or 6.4 L s⁻¹. Using a large range of values for δ¹⁸Ow_f between −20.0‰ and −15.5‰ produces a relatively small range in Fw (4.2−7.6 L s⁻¹). This range is just slightly less than the 8.5 L s⁻¹ measured at the mouth of Alluvium Creek in late August of 1998 by Gemery-Hill et al. (2007). Thus the observed δ¹⁸O shift in Brimstone Basin surface
waters can be plausibly linked to upflow of CO₂ from warm but sub-boiling thermal water at depth.

Annual precipitation (~100 cm) and recharge estimates (5–30 cm) from Kharaka et al. (2002) for the Brimstone Basin area yield a range of 1.7–10.5 L s⁻¹ for the annualized throughput of shallow groundwater for a 1.1 km² area. The average throughput of 6.1 L s⁻¹ is close to our calculated throughput of 6.4 L s⁻¹ based on ¹⁸O in water of −18.4‰. Considering a range of −20.0‰ and −15.5‰ for ¹⁸O in water, the temperature range calculated for the deep thermal water is 93 ± 19 °C (Fig. 11).

We find no evidence that the oxygen isotope shift in the water is due to reactions involving SO₄, which at Brimstone Basin forms mainly from microbial oxidation of S in the shallow subsurface (Knickerbocker et al., 2000; Nordstrom et al., 2009). Not only is oxygen exchange between H₂O and SO₄ very slow at low temperature (McKenzie and Truesdell, 1977), but the export of SO₄ from the basin is many orders of magnitude less than the diffuse CO₂ discharge and the water outflow; e.g., the SO₄ load at the mouth of Alluvium Creek (in August 1998) was only −0.006 Mmol d⁻¹ (Gemery-Hill et al., 2007). Even if all of the SO₄ had a δ¹⁸O value of 30‰ (Fritz et al., 1989; Brunner et al., 2005), only −0.04 L s⁻¹ of shallow groundwater could be shifted 3.5‰. In addition, the amount of the oxygen shift in each sample does not correlate with SO₄ concentration (Fig. 8b). Oxygen-shifted waters have all acquired >1000 mg L⁻¹ SO₄, but a sample from Alluvium Creek with SO₄ ~ 2500 mg L⁻¹ is not shifted (Ball et al., 2001) and two samples with the highest SO₄ concentrations (Nordstrom et al., 2009) do not have the greatest oxygen shift.

6. Summary

This study at Brimstone Basin provides the first estimate of CO₂ emissions from a large-scale survey of cold degassing at Yellowstone National Park. Our findings indicate that significant amounts of magmatic CO₂ (about −277 t d⁻¹) with lesser H₂S (0.6 t d⁻¹) discharge diffusely through the altered ground. Diffuse gas flux is clearly the main component of the magmatic volatile efflux from Brimstone Basin. The acidic nature and small discharge of the creeks that drain the basin preclude a significant flux of dissolved magmatic carbon. The 3 sample sites where gas bubbled up through water were the only focused gas vents that we observed.

The early description by the Washburn Expedition suggested that volcanic activity was waning at Brimstone Basin (Langford, 1905) and more recent research has suggested that the last geothermal activity may have occurred hundreds to thousands of years ago (Knickerbocker et al., 2000). Our findings from isotopic indicators and gas geochemistry indicate that although there are no surface thermal anomalies, a clear connection to a heat source remains. Notably, the shift in δ¹⁸O from isotopic indicators and gas geochemistry indicate that significant amounts of degassing areas near Mud Volcano (Tercek et al., 2008) suggest that cold emissions may be a significant component of the total CO₂ output from Yellowstone.

Acknowledgments

Cynthia Werner suggested we visit Brimstone Basin after finding significant CO₂ efflux during a reconnaissance gas emission flight. Our work is funded by the U.S. Geological Survey Volcano Hazards Program. We thank Dan Mahony and Christie Hendrix (U.S. National Park Service, Yellowstone National Park) for field support and other logistical help. Isotopic and chemical analyses were provided by several USGS laboratories, Andy Hunt (³He/²⁰Ne) and Pat Shanks (³⁴S and δ¹⁸O), (Denver, CO) and Kinga Revesz (δ¹³C), Reston VA; Mark Hubner (anion chemistry, Menlo Park, CA). Our field party also included Allison Phillips, (Washington State University).

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