

## Oxidation reactions for reduced Fe, As, and S in thermal outflows of Yellowstone National Park: biotic or abiotic?

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**ABSTRACT:** Oxidation reactions for S, As, and Fe have been measured downstream in several hot spring discharges at Yellowstone National Park. Oxidation of dissolved  $\text{H}_2\text{S}$  to  $\text{S}_2\text{O}_3$  is the fastest reaction and occurs abiotically and nearly instantaneously on exposure to air. In high pH overflows ( $\text{pH} > 7$ ),  $\text{S}_2\text{O}_3$  shows little tendency to oxidize further. In low pH overflows,  $\text{S}_2\text{O}_3$  disproportionates, producing elemental sulfur and sulfite. Solid sulfur is then oxidized more slowly to sulfuric acid by microbial catalysis. Oxidation of dissolved  $\text{As}^{\text{III}}$  to  $\text{As}^{\text{V}}$  and  $\text{Fe}^{\text{II}}$  to  $\text{Fe}^{\text{III}}$  in acid waters ( $\text{pH} = 2.7$ ) requires microbial catalysis and proceeds at rates comparable to those in acid mine drainage. The oxidation rate for  $\text{Fe}^{\text{II}}$  is about 2 mmol/L/h and for  $\text{As}^{\text{III}}$  is about 0.07 mmol/L/h, both of which are many orders of magnitude faster than the abiotic rate.

### 1 INTRODUCTION

Geothermal waters rising from depths contain reduced forms of iron [ $\text{Fe}^{\text{II}}$ ], arsenic [ $\text{As}^{\text{III}}$ ], and sulfur [ $\text{S}^{\text{II-}}$ ]. Dissolved sulfur can occur as both  $\text{H}_2\text{S}$  and  $\text{SO}_4^{\text{-}}$  but dissolved iron and arsenic occur only in their reduced forms until they are exposed to oxygen by mixing with air or with oxygenated ground waters. Oxidation sets up strong redox gradients and affects the chemical behavior of the redox elements. In thermal overflows the oxidation gradient is often the zone of abundant microbial growth. Rates of oxidation-reduction reactions are commonly controlled by microbial processes rather than by abiotic processes but distinguishing between the two types can be difficult. This study describes examples of oxidation of  $\text{Fe}^{\text{II}}$ ,  $\text{As}^{\text{III}}$ , and  $\text{S}^{\text{II-}}$  in Nymph Creek and Ojo Caliente thermal overflows in Yellowstone National Park, discusses their rates, and abiotic vs. biotic oxidation mechanisms, and discusses similar mechanisms deduced from data from other springs.

### 2 FIELD SITES AND METHODS

#### 2.1 Nymph Creek

Nymph Creek is located along the roadside just north of Norris Geyser Basin, where there are several small hot springs (Fig. 1). The main source of Nymph Creek thermal water comes from a small discharge in a crack in silica sinter at a pH of 2.7–3.0, a

temperature of 60–62°C; the main constituents are  $\text{SiO}_2$  (240 mg/L),  $\text{SO}_4$  (300 mg/L), Na (70 mg/L), K (45 mg/L) and Cl (35 mg/L). Dissolved sulfide is rarely detectable,  $\text{Fe}^{\text{T}}$  is about 3 mg/L and  $\text{As}^{\text{T}}$  is about 0.1 mg/L. A transect was chosen in the overflow to define the rate of iron and arsenic

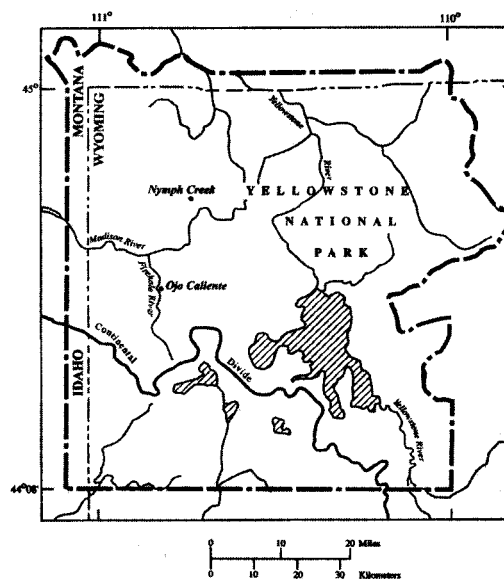


Figure 1. Location of sampling areas in Yellowstone Park.

oxidation from the gradient in concentration and travel time.

## 2.2 Ojo Caliente

Ojo Caliente is located next to the Firehole River in Lower Geyser Basin (Fig. 1). It discharges into a large pool at the boiling temperature ( $\sim 93^\circ\text{C}$  at that altitude) and drains into 4 distinct channels. Two of these channels were chosen to represent the range of flow from fastest to slowest. The slowest flow channel is also the longest. The pH at Ojo begins at about 7.5 and increases to about 8.5 due to  $\text{CO}_2$  degassing. The water composition is dominated by Na (330 mg/L), Cl (300 mg/L),  $\text{HCO}_3^-$  (235 mg/L) and  $\text{SiO}_2$  (240 mg/L). Concentrations of Fe are usually at or below detection ( $<0.002$  mg/L) and  $\text{H}_2\text{S}$  concentrations vary from 0.3 to 1 mg/L. Concentrations of dissolved As are about 1 mg/L.

## 2.3 Analytical methods

A mobile laboratory truck containing an ion chromatograph, UV-visible spectrophotometer, auto-titrator, and reagent-grade water system was parked close to each sampling site so that unstable species such as redox species of Fe and intermediate sulfur oxyanions could be determined as soon as possible after collection. Samples for the determination of  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{T}}$ ,  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{T}}$ , and intermediate sulfur species were filtered by pumping from the source with a portable peristaltic pump fitted with medical-grade silicone tubing through a 142-mm diameter all-plastic filter holder (Kennedy et al. 1976) containing a 0.1- $\mu\text{m}$  mixed-cellulose-ester filter membrane.

Stabilizing reagents for intermediate sulfur species were put into the sample bottle before the sample was collected. Samples for  $\text{H}_2\text{S}$  determination were collected directly into a plastic syringe to minimize the inclusion of atmospheric air, then forced through a syringe-mounted 0.45- $\mu\text{m}$  membrane filter. Samples were filtered directly into a measuring cuvette in which the appropriate reagents were quickly mixed. Total lag time between sampling and analysis was less than 20 seconds.

Concentrations of  $\text{H}_2\text{S}$  were determined by measuring absorbance using a Hach DR/2000 field spectrophotometer using Hach Method 8131, which is based on the APHA (1985) methylene blue method. Thiosulfate and  $\text{S}_x\text{O}_6$  were determined (after removal of  $\text{H}_2\text{S}$  with addition of  $\text{ZnCl}_2$  and  $\text{NaOH}$ ) by syringe-filtering the sample directly into the ion chromatograph on-site in the mobile laboratory. Iron(total) and  $\text{Fe}^{\text{II}}$  concentrations were determined using a colorimetric method based on the FerroZine method of Stookey (1970), as modified by To et al. (1999). Arsenic(total) and  $\text{As}^{\text{III}}$  concentrations were

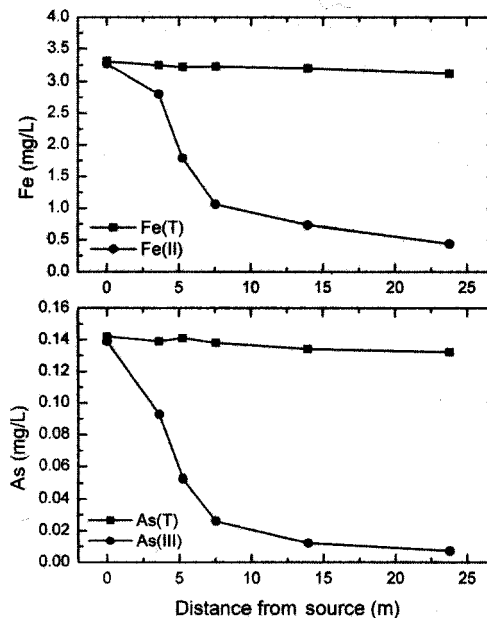


Figure 2. Iron and arsenic oxidation with distance along Nymph Creek.

determined by hydride generation atomic-absorption spectrometry using a Perkin-Elmer AAnalyst 300 atomic absorption spectrometer in absorption mode with a FIAS-100 flow injection analysis system hydride generator, quartz cell, and furnace.

## 3 RESULTS

### 3.1 Nymph Creek

Both Fe and As were found to oxidize rapidly upon exposure to the atmosphere (Fig. 2). The transect was resampled after dark. Similar results were obtained, indicating that photocatalysis was not significant in the first 15 m.

### 3.2 Ojo Caliente

At Ojo Caliente,  $\text{H}_2\text{S}$  was found to oxidize and volatilize rapidly upon exposure to the atmosphere in the overflow (Fig. 3). Dissolved oxygen increases from below detection ( $<0.1$  mg/L) to more than 3.5 mg/L in the longer channel (that also reaches lower temperatures of about  $50^\circ\text{C}$  before entering the Firehole River). Thiosulfate concentrations increase quantitatively with the decrease in  $\text{H}_2\text{S}$ . Most other major and trace constituents undergo little change other than small evaporative concentration effects. Arsenic undergoes some oxidation in the longer channel but does not oxidize in the faster one.

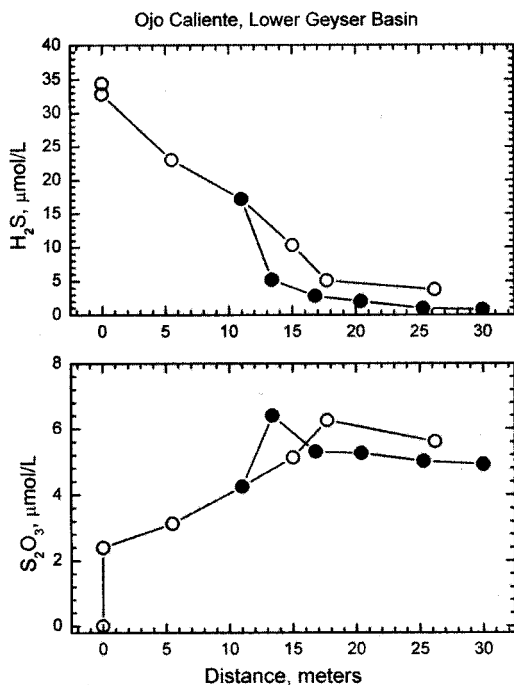


Figure 3. Oxidation of H<sub>2</sub>S and formation of S<sub>2</sub>O<sub>3</sub> with distance in 2 channels of Ojo Caliente overflow. Closed symbols show the separation of values for channel with slower and longer flow.

Measurements of H<sub>2</sub>S oxidation in acid hot springs, such as Frying Pan Spring, have shown that thiosulfate does form but is quickly degraded to elemental sulfur making the pool turbid (Ball et al. 1998; Xu et al. 1998). Oxidation of the resultant colloidal sulfur forms sulfuric acid, keeping Frying Pan Spring at a pH of about 2.3.

#### 4 DISCUSSION

The steady-state redox profiles for the oxidation of iron, arsenic, and sulfur species in thermal overflows can be combined with travel times to determine oxidation rates. The theoretical framework is the reactive-advective equation for steady flow:

$$\left(\frac{\partial c}{\partial t}\right)_x = 0 \quad \text{and} \quad \left(\frac{v\partial c}{\partial x}\right)_t = r$$

where  $c$  is concentration of a constituent,  $t$  is time,  $x$  is distance,  $v$  is velocity, and  $r$  is reaction rate. Although the concentration does not change at one location with time, it does change from one location to the

next such that by finite difference:

$$\frac{v\Delta c}{\Delta x} = \frac{\Delta x\Delta c}{\Delta t\Delta x} = \frac{\Delta c}{\Delta t} = r$$

Hence, by measuring the travel time from station to station (=velocity) and the concentration from station to station in an overflow transect, the oxidation rate can be calculated for any given redox species. This method also assumes zero-order reaction rate, which is not exactly valid. The difference between linear and non-linear rates, however, is not large when comparing microbial and abiotic rates. Applying this method to the arsenic and iron oxidation in Nymph Creek, the oxidation rate of Fe<sup>II</sup> is about 2 mmol/L/h. For As<sup>III</sup>, the oxidation rate is about 0.07 mmol/L/h. These rates compare to the inorganic rates (at 25°C) of 10<sup>-5</sup> mmol/L/h for Fe<sup>II</sup> and <10<sup>-8</sup> mmol/L/h for As<sup>III</sup> (see Nordstrom 2003). Hence, microbial catalysis increases iron oxidation rates in the field by more than 5 orders of magnitude and increases arsenic oxidation by more than 9 orders of magnitude.

Other measured field rates for microbial iron oxidation are similar. The Fe<sup>II</sup> oxidation rates are 1–12 mmol/L/h for *in situ* and they are even higher for engineered bioreactors (Nordstrom 2003). Microbial arsenite oxidation has more commonly been reported as doubling time and less commonly as a half-life for As<sup>III</sup>, the appropriate form for exponential (or first order) change. Nevertheless, Gihring & Banfield (2001) observed arsenite oxidation in the lab by a Yellowstone isolate, *Thermus* HR 13, at about 0.12 mmol/L/h, very similar to the rates reported here.

These rates of iron and arsenic oxidation are clearly microbially mediated. Oxidation of H<sub>2</sub>S, however, appears to be dominated by abiotic mechanisms until elemental S or thiosulfate is formed. The rate of thiosulfate formation for the data from Ojo Caliente is 0.16 mmol/L/h and for lab studies the value is about 0.003 mmol/L/h at 25°C (Chen & Morris 1972; O'Brien & Birkner 1977). Although the *in situ* rate is about 50 times faster in the field, the temperature is also nearly 70° higher. At temperatures where few microbes can survive, the oxidation of H<sub>2</sub>S to S<sub>2</sub>O<sub>3</sub> is instantaneous. At Angel Terrace our data shows instantaneous formation of 4 μmol/L S<sub>2</sub>O<sub>3</sub> from H<sub>2</sub>S in less than a second. Data on H<sub>2</sub>S oxidation in abiotic lab studies show a substantial increase in rate constants with increasing temperature that can account for the increase observed for our Yellowstone field rates (Zhang & Millero 1994).

For Ojo Caliente an estimate of the quantity of H<sub>2</sub>S oxidized vs. the amount volatilized can be made. Of the original 30 μmol/L H<sub>2</sub>S in the Ojo pool, 10 μmol/L was converted to S<sub>2</sub>O<sub>3</sub> only. The remaining 20 μmol/L must have been volatilized. Hence, for a hot spring at boiling temperature and with a pH of

about 7.7, about 2/3 of the original H<sub>2</sub>S is volatilized and about 1/3 stays in the water as S<sub>2</sub>O<sub>3</sub>.

## 5 CONCLUSIONS

Both biotic and abiotic mechanisms are operative during the oxidation of redox-sensitive elements in thermal overflows. For iron and arsenic, oxidation in acid springs is catalyzed by iron and arsenic oxidizing microbes that can increase the oxidation rate by many orders of magnitude. For H<sub>2</sub>S oxidation, rapid abiotic oxidation to thiosulfate and elemental sulfur occurs followed by the slower oxidation of sulfur and thiosulfate to sulfuric acid. For one circumneutral pH hot spring, Ojo Caliente, the first estimate has been made of the quantity of H<sub>2</sub>S volatilized (67%) and the remaining dissolved H<sub>2</sub>S (33%) quantitatively converts to S<sub>2</sub>O<sub>3</sub>.

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