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# Sulfur geochemistry of hydrothermal waters in Yellowstone National Park, Wyoming, USA. II. Formation and decomposition of thiosulfate and polythionate in Cinder Pool

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## Abstract

Cinder Pool is an acid-sulfate-chloride boiling spring in Norris Geyser Basin, Yellowstone National Park. The pool is unique in that its surface is partially covered with mm-size, black, hollow sulfur spherules, while a layer of molten sulfur resides at the bottom of the pool (18 m depth). The sulfur speciation in the pool was determined on four different days over a period of two years. Samples were taken to evaluate changes with depth and to evaluate the importance of the sulfur spherules on sulfur redox chemistry. All analyses were conducted on site using a combination of ion chromatography and colorimetric techniques.

Dissolved sulfide ( $\text{H}_2\text{S}$ ), thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ), polythionates ( $\text{S}_x\text{O}_6^{2-}$ ), and sulfate were detected. The polythionate concentration was highly variable in time and space. The highest concentrations were found in surficial samples taken from among the sulfur spherules. With depth, the polythionate concentrations dropped off. The maximum observed polythionate concentration was  $8 \mu\text{M}$ . Thiosulfate was rather uniformly distributed throughout the pool and concentrations ranged from 35 to  $45 \mu\text{M}$ . Total dissolved sulfide concentrations varied with time, concentrations ranged from 16 to  $48 \mu\text{M}$ . Sulfate was relatively constant, with concentrations ranging from 1150 to  $1300 \mu\text{M}$ . The sulfur speciation of Cinder Pool is unique in that the thiosulfate and polythionate concentrations are significantly higher than for any other acid-sulfate spring yet sampled in Yellowstone National Park. Complementary laboratory experiments show that thiosulfate is the intermediate sulfoxyanion formed from sulfur hydrolysis under conditions similar to those found in Cinder Pool and that polythionates are formed via the oxidation of thiosulfate by dissolved oxygen. This last reaction is catalyzed by pyrite that occurs as a minor constituent in the sulfur spherules floating on the pool's surface. Polythionate decomposition proceeds via two pathways: (1) a reaction with  $\text{H}_2\text{S}$ , yielding thiosulfate and elemental sulfur; and (2) by disproportionation to sulfate and thiosulfate.

This study demonstrates that the presence of a subaqueous molten sulfur pool and sulfur spherules in Cinder Pool is of importance in controlling the pathways of aqueous sulfur redox reactions. Some of the insights gained at Cinder Pool may be relevant to acid crater lakes where sulfur spherules are observed and variations in polythionate concentrations are used to monitor and predict volcanic activity. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Cinder Pool; sulfur redox chemistry; polythionate; Yellowstone N.P.

## 1. Introduction

Cinder Pool is one of the most unique springs among the more than 10,000 hydrothermal features

in Yellowstone National Park (YNP). The most striking features of this boiling acid-sulfate-chloride spring at Norris Geyser Basin are the partial coverage of its surface by black hollow sulfur spherules—generally known as “cinders”—and the subaqueous molten sulfur pool at a depth of about 18 m and a

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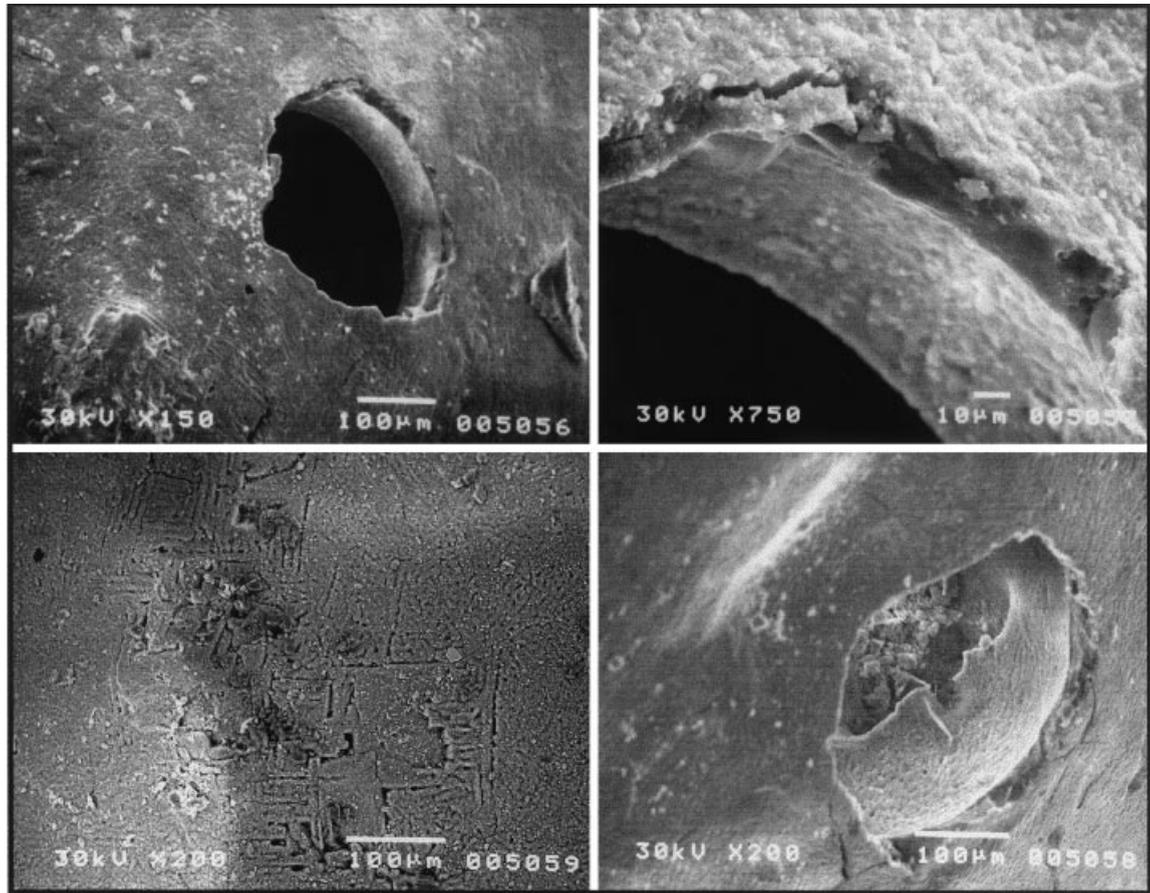


Fig. 1. SEM image of part of a sulfur spherule found floating on Cinder Pool, Yellowstone National Park. Sulfur spherules are hollow and perforated with holes. Spherules are typically about 5 mm in diameter.

temperature of 120°C (White et al., 1988). Furthermore, the acid water of Cinder Pool has a unique aqueous sulfur speciation. Out of 39 hydrothermal waters analyzed by Xu et al. (1998), it is the only water which contains detectable polythionate (up to 8  $\mu\text{M}$ ) and it is the only spring with  $\text{pH} < 5$  that contains thiosulfate at a significant concentration (up to 45  $\mu\text{M}$ ).

The floating sulfur spherules and subaqueous molten sulfur pool are features rarely seen in hot springs. The floating sulfur spherules are formed by gas discharges through, or from, the molten sulfur layer at the bottom of Cinder Pool. When gas passes through the layer, liquid sulfur encapsulates the bubbles. As the encapsulated bubbles separate from the molten sulfur layer and enter the overlying boiling

aqueous solution, the sulfur solidifies and traps the gas. The trapped gas makes the spherules buoyant. As the spherules rise, the trapped gas expands and small holes are formed in the spherules (see Fig. 1). The only other reported example of its kind is Whangioteangi Spring at Waiotapu hydrothermal area in New Zealand (Lloyd, 1959). Floating sulfur spherules are, however, not uncommon in crater lakes at the summits of active volcanoes (Bennett and Raccichini, 1978; Francis et al., 1980; Oppenheimer and Stevenson, 1989; Hurst et al., 1991; Takano et al., 1994b). Few hot-spring waters contain detectable polythionate (e.g. Wilson, 1959; Gundlach, 1965; Xu et al., 1998), but in acid crater lakes polythionates are common minor or trace constituents (Day and Allen, 1925; Wilson, 1941; Takano, 1987; Takano and Watanuki,

Table 1  
Chemical analysis of Cinder Pool, Yellowstone National Park (mg/l)<sup>a</sup>

Ca	Mg	Na	K	SO <sub>4</sub>	F	Cl	SiO <sub>2</sub>	B	Li
5.9	0.024	373	57.6	96	6.24	601	433	9.60	4.70
S <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> S	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Al	Fe <sub>tot</sub>	Fe(II)	Sr	Br	As <sub>tot</sub>
5.10	1.6	1.63	18	1.13	0.088	0.088	0.011	1.7	2.4

<sup>a</sup> Sample collected 8/22/95, sample code 95WA110; pH = 4.22; T = 95°C, Specific Conductance = 2320 microS cm<sup>-1</sup>.

1990; Rowe et al., 1992; Pasternack and Varekamp, 1994; Takano et al., 1994a,b). Thiosulfate, on the other hand, has been detected in hot-spring waters of many active hydrothermal systems world wide (e.g. Allen and Day, 1935; Gundlach, 1965; Boulegue, 1978; Subzhiyeva and Volkov, 1982; Webster, 1987, 1989; Veldeman et al., 1991; Migdisov et al., 1992), but not in crater-lake waters (Takano et al., 1994a). While there are significant differences between Cinder Pool (pH 4) and most acid crater lakes (pH < 2), the unique physical and chemical characteristics of Cinder Pool constitutes a setting that provides insights into processes controlling sulfur speciation in acid waters that may improve our understanding of the sulfur chemistry of acid crater lakes.

Cinder Pool provides a rare opportunity to study reactions relevant to acid crater lakes under less dangerous and logistically easier conditions than are typically encountered in and around acid crater lakes associated with active volcanoes. Cinder Pool provides a particularly good opportunity to investigate how aqueous sulfur species are influenced by the presence of a subaqueous molten sulfur pool and floating sulfur spherules. The transformations of sulfur species in such a complicated heterogeneous system are of geologic interest. Subaqueous molten sulfur pools have been suggested to play a role as traps for heavy metals convected through heat pipes, which have been postulated as metal-transferring or metal-depositing regimes in hydrothermal systems (Giggenbach, 1987; Christenson and Wood, 1993). Perhaps most important to human safety is the notion that changes in polythionate concentrations in crater lakes can be used as an indicator of impending phreatic eruptions of volcanoes (Takano, 1987; Takano and Watanuki, 1990; Rowe et al., 1992; Takano et al., 1994a; Zheng and Takano, 1996). In addition, thiosulfate has been suggested to be an important ligand

for precious-metal transport in hydrothermal solutions (Webster, 1986; Kucha, 1988; Benedetti and Boulegue, 1991; Kucha and Viaene, 1993; Kucha et al., 1995). Hence, it is important to understand the formation and decomposition of thiosulfate and polythionates in hydrothermal systems and crater lakes.

This study, as a part of a comprehensive investigation into the geochemistry of intermediate sulfoxyanions in hydrothermal systems, examines the formation and decomposition of thiosulfate and polythionate in Cinder Pool, with an emphasis on the role of the molten sulfur pool and the floating sulfur spherules. In this study, we present the results of three field studies in which sulfur speciation was determined on site. Furthermore, complementary field and laboratory experiments were conducted to determine: (1) the composition of waters in contact with elemental sulfur (sulfur hydrolysis); (2) the rate of polythionate formation via oxidation of thiosulfate in the presence of the sulfur spherules; (3) the in situ decomposition rate of polythionates in the absence of the spherules in Cinder Pool; and (4) the decomposition rate of polythionate via its interaction with hydrogen sulfide. The laboratory experiments were conducted at conditions relevant to those at Cinder Pool. Based upon the field studies and experimental results, a model for the transformation of sulfur species in Cinder Pool is presented. The general geochemical properties and sulfur speciation of Cinder Pool and other representative YNP waters are summarized in Ball et al. (1998) and Xu et al. (1998), respectively. A chemical analysis for Cinder Pool is shown in Table 1.

The geology and thermal activity of Norris Geyser Basin have been reported in White et al. (1988), while the geochemistry of thermal waters and the origin of various water types at Norris Geyser Basin have been presented by Fournier and co-workers (Fournier et al., 1992, 1998). Photographs of Cinder Pool and the cinders are available for viewing on a

webpage maintained by Schoonen's laboratory (<http://sbmp97.ess.sunysb.edu/>).

## 2. Previous work

The floating spherules at Cinder Pool were first described by Allen and Day (1935). They reported that the spherules consist of elemental sulfur blackened by dispersed pyrite. The presence of the spherules at Cinder Pool as well as the pool of molten sulfur at the bottom has been described and documented with pictures by White et al. (1988). In their report, White et al. (1988) present also a chemical analysis for Cinder Pool, as well as a geological, hydrogeological, and geochemical framework for the entire Norris Geyser Basin. Zinder and Brock (1977) included Cinder Pool in a comprehensive study of SO<sub>2</sub> and dissolved sulfur concentrations in YNP waters. For Cinder Pool they reported a sulfite concentration of 1.5 μM and a elemental sulfur concentration of 528 μM.

As noted before, sulfur spherules are reasonably common features in acid crater lakes. The sulfur spherules at Ijen crater lake of Indonesia, Bannoe Lake of Uzon Caldera in Kamchatka, and Yugama crater lake at Kusatsu-Shirane volcano of Japan have been described by Delmelle and Bernard (1994), Takano et al. (1994b) and Delmelle et al. (1996), respectively. The sulfur spherules at these crater lakes generally contain several weight percent iron sulfide, mainly pyrite, and minor heavy metal sulfide, such as bismuthinite (Cu<sub>2</sub>FeSnS<sub>4</sub>), Sb-rich enargite (Cu<sub>3</sub>AsS<sub>4</sub>) and stannite (Cu<sub>2</sub>FeSnS<sub>4</sub>). Takano et al. (1994b) studied the mineralogy and geochemistry of subaqueous molten sulfur at Yugama crater lake, and found that the sulfur contains homocyclic sulfur (S<sub>x</sub>, 6 ≤ x ≤ 16) and probably sulfane monosulfonates (HS<sub>8</sub>SO<sub>3</sub>H).

The polythionates in acidic crater lakes are believed to be generated from the aqueous interaction between SO<sub>2</sub> and H<sub>2</sub>S gases discharged from subaqueous fumaroles, and decomposed by sulfitolysis and hydrolysis interaction (Takano, 1987). The formation of thiosulfate in hydrothermal solutions, on the other hand, has been attributed to hydrolysis of elemental sulfur by hydrothermal waters (Webster, 1987; Xu et al., 1998). The hydrolysis of elemental sulfur at

elevated temperature has been known to produce dissolved sulfide (H<sub>2</sub>S and HS<sup>-</sup>) and sulfoxyanions. The type of sulfoxyanions formed as a result of sulfur hydrolysis depends on temperature and pH. In acid solutions, the dominant sulfoxyanion is sulfate, while in neutral and alkaline solutions thiosulfate dominates (Oana and Ishikawa, 1966; Ellis and Giggenbach, 1971; Robinson, 1973) (cf. pH of Cinder Pool is 4). Furthermore, recently Xu and Schoonen (1995) and Xu et al. (1996) demonstrated in laboratory experiments that pyrite and other semiconducting metal sulfides can catalyze the oxidation of thiosulfate to tetrathionate, while elemental sulfur cannot catalyze this reaction. This suggests that the floating sulfur spherules, which contain pyrite and possibly other metal sulfides, may catalyze the formation of polythionates in hot springs such as Cinder Pool and in acid crater lakes.

## 3. Research methods

In this study, both field work and laboratory studies were undertaken. The sampling and analysis methods used in the field, as well as the methods used in the field and laboratory experiments are described separately. Preservation of thiosulfate over extended periods of time is a serious problem (Xu et al., 1998). To minimize changes in sulfoxyanion speciation upon prolonged storage all water samples from Cinder Pool were analyzed within about 2 hours in a mobile lab operated and maintained by the USGS. For this study, the mobile lab was stationed on the parking lot at Norris Geyser Basin, about a 20-min walk from Cinder Pool.

### 3.1. Mineralogical and chemical analysis of cinders

About a hundred grams of floating cinders were collected in amber bottles and polyethylene bottles. To minimize possible oxidation of the cinders, the bottles were filled up with water from the pool. A fraction of the sample was dried, crushed, and 10 g was submitted to ActLabs, Canada for major- and trace-element analysis. (The use of firm, trade, and brand names is for identification purposes only and does not constitute endorsement by the US Government.) A second fraction was used for determination of the mineralogical composition. The mineralogy of

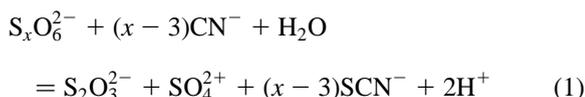
the raw sample and of the fraction not dissolvable in CS<sub>2</sub> was determined using powder X-ray diffractometry (Scintag). The iron content of the concentrate was determined using a colorimetric technique after acid digestion. To study the morphology of the cinders as well as the distribution of non-sulfur minerals in cinders, a few spherules were examined using Scanning Electron Microscopy (SEM).

### 3.2. Water sampling and analyses

Xu et al. (1998) details of sampling, preservation, and analysis of aqueous sulfoxyanions in hot spring waters. In brief, near-surface samples of Cinder Pool were drawn into a 60-ml plastic syringe fitted with a 20-cm section of Teflon tubing, and then pressure-filtered through a 0.45- $\mu$ m syringe filter into a sampling bottle. Samples from depth were collected using two different techniques. One set of samples was collected by lowering a Tygon™ tube to the desired depth. Samples were then withdrawn by connecting the tube to a Cole-Palmer Masterflex™ peristaltic pump. The solution was pressure-filtered through a 0.45- $\mu$ m membrane and collected in a sample bottle. Alternatively, samples from depth were collected by dipping a stainless steel thermos can attached to an aluminum pole to the desired depth. Samples were then immediately withdrawn from the thermos using the same sampling technique as used for the surficial samples. To determine thiosulfate concentration, samples were collected into 30-ml amber glass bottles containing 1 ml of 1 M ZnCl<sub>2</sub> solution. Samples for polythionate analysis were collected in 30-ml amber glass bottle containing 1 ml of a 1 M ZnCl<sub>2</sub> solution, 1 ml of a 1 M NaOH solution, and 1 ml of a 1 M KCN solution. The bottles were immediately put on ice until analysis. The analysis for the sulfoxyanions was typically conducted one to two hours after collection. For total dissolved sulfide determinations (S(-II)), an untreated aliquot of the sample was taken and immediately analyzed using Hach method 8131. This method is based on the methylene blue method. The dynamic range of this technique covers concentrations from 0.1 to 20  $\mu$ M. Some samples had S(-II) concentrations in excess of 20  $\mu$ M and were diluted with deionized water.

At the mobile lab, an aliquot of preserved sample

was drawn into a syringe and injected into an Dionex 2010i/2000i ion chromatograph through a slip-on syringe filter (0.45  $\mu$ m pore-size). Polythionate concentrations and average chain lengths were determined using alkaline cyanolysis (see Xu et al., 1998, for details). The cyanolysis of polythionate generates thiocyanate and thiosulfate according to:



where  $x \geq 4$ . Hence, with this method the trithionate concentration cannot be determined. The total polythionate concentration ( $x \geq 4$ ) is determined from the difference in thiosulfate concentration between the cyanolyzed and uncyanolyzed samples; while the average chain length is determined from the resulting thiocyanate and thiosulfate concentration. Using two AG4A guard columns in series, in combination with a standard NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> eluent, and a conductivity detector, thiosulfate and thiocyanate can be determined within 6 min. The detection limits for thiosulfate and thiocyanate are 0.1 and 0.5  $\mu$ M, respectively. Sulfate concentrations were measured using standard ion chromatographic techniques (AS4A column with NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> eluent).

### 3.3. In situ polythionate stability experiment

To evaluate the stability of polythionate in Cinder Pool, an in situ polythionate stability experiment was carried out. Five surficial water samples were collected from a section of the pool covered with spherules, the water was separated from the sulfur spherules by filtration over a 0.45- $\mu$ m filter, the filtrate was collected in 60-ml glass bottles, and these bottles were resuspended in the pool. The purpose for resuspension in pool was to keep the solutions at temperature. Periodically, one of the samples was retrieved from the pool, and NaOH and KCN were added for total polythionate determination at the mobile lab.

### 3.4. Polythionate reactivity with H<sub>2</sub>S laboratory experiment

The aqueous sulfur speciation determined in the field suggests that polythionate may be decomposed by the interactions involving H<sub>2</sub>S in Cinder Pool (see

Section 4). Although it is well known that in alkaline solutions S(-II) can degrade polythionate to thiosulfate quantitatively and spontaneously (Lyons and Nickless, 1968), the reactivity of polythionate with H<sub>2</sub>S in acidic solutions has not been investigated in detail. Takano et al. (1994a) reported the results of an experimental study that addresses this issue, but few experimental details were provided. In this study, the decomposition of polythionate by acid H<sub>2</sub>S solutions was examined by monitoring the formation of thiosulfate. To avoid the thermal decomposition of polythionate (Meyer and Ospina, 1982), the experiment was carried out at 20°C in a HCl solution of pH 1.0. To minimize the volatilization of H<sub>2</sub>S, the experiments were conducted in 60-ml plastic syringes. The starting polythionate solutions, which were prepared by dissolving sodium tetrathionate into a 0.1 M HCl solution, were drawn into a syringe preloaded with the desired amount of sodium sulfide, and then the concentration of thiosulfate formed from the polythionate–H<sub>2</sub>S interaction was monitored as a function of time.

### 3.5. Sulfur hydrolysis laboratory experiment

Sulfur hydrolysis experiments were conducted at temperatures of 100, 120 and 150°C. The experiments at 120 and 150°C were carried out in a 1-l, quartz-glass lined, 316 ss stirred autoclave (Autoclave Engineers™). The reaction vessel, pre-loaded with 0.8 g elemental sulfur, was evacuated, then loaded with 800 ml of deionized water. Prior to injection into the vessel, the water was purged with N<sub>2</sub> for an hour to remove dissolved oxygen. The pH of the solution was buffered by keeping the system under a constant CO<sub>2</sub> pressure. The high-temperature pH values, around pH 4, were calculated from the P<sub>CO2</sub> (Xu, 1997). After heating the vessel to the desired temperature within 1–2 h, the vessel was kept at a constant temperature for the duration of the experiment. Periodically, an aliquot of the solution was withdrawn from the autoclave and analyzed for sulfate, sulfite and thiosulfate using the same analytical techniques used in the field.

The experiments at 100°C were conducted in boiling water at atmospheric pressure. The experiments were conducted in 1-l Erlenmeyer flasks; no attempt was made to exclude atmospheric oxygen from the flasks during the experiment. The water was, however, boiled for 30 min before sulfur was added.

Experiments were conducted at pH values of 4.0, 6.0, and 8.0. The desired initial pH was obtained by adding small amounts of a 0.1 mM HCl or NaOH solution. During the course of the experiment the pH of the solution was kept constant (within 0.2 pH unit from the initial pH value) by adding small amounts of a 0.1 M NaOH solution. The effect of boiling on the sulfoxyanion concentration was corrected by normalizing the measured concentration to the chloride concentration (Cl<sup>-</sup> determined by ion chromatography along with sulfate for each sampling point).

### 3.6. Thiosulfate oxidation laboratory experiment

The experiments of thiosulfate oxidation in the presence of sulfur spherules were conducted in a 125-ml glass flask loaded with 1.0 g crushed sulfur spherules in a water bath kept at 20, 50 and 90°C. The starting solution was a 100-ml, 0.5 mM thiosulfate solution prepared by dissolving reagent-grade Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O in an 0.1 M acetic acid–sodium acetate buffer (pH = 4.0 at 20°C) saturated with air. The solution was in contact with air during the experiment and constantly stirred magnetically. The concentrations of thiosulfate and polythionate were determined as a function of time.

## 4. Results

### 4.1. Mineralogical and chemical characteristics of cinders

While most cinders are spherules with diameters up to 5 mm, some are irregular in shape. All cinders are black, hollow, and perforated with small holes (see Fig. 1). CS<sub>2</sub>-soluble sulfur makes up 94.2–95.1% of the sulfur spherules, and orthorhombic sulfur is the predominant mineral phase. This high sulfur content is responsible for the 95.06% Loss On Ignition reported in Table 2. The residue insoluble in CS<sub>2</sub> contains 22.2–22.9% iron. Pyrite is the predominant Fe-containing mineral phase in the CS<sub>2</sub>-insoluble residue. Hence, the pyrite content of the sulfur spherules is about 2%. SEM back-scatter images indicate that pyrite appears homogeneously dispersed in cinders, not as a coating on the spherules surfaces.

The chemical analysis of the cinders collected from Cinder Pool is summarized in Table 2. The results

Table 2  
Chemical analysis of cinders, Cinder Pool, Yellowstone National Park

Constituent	wt%	Constituent	ppm	Constituent	ppm
SiO <sub>2</sub>	2.52	Ba	16	Co	2.8
Al <sub>2</sub> O <sub>3</sub>	0.26	Sr	6	Cr	4.8
Fe <sub>2</sub> O <sub>3</sub>	1.87	Y	24	Mo	142
MnO	< 0.01	Zr	227	Sb	320
MgO	0.01	V	3	Se	2.5
CaO	0.06	Cu	9		
Na <sub>2</sub> O	< 0.01	Pb	37	Au	129 (ppb)
K <sub>2</sub> O	0.03	Zn	70		
TiO <sub>2</sub>	0.09	Ag	< 0.4		
P <sub>2</sub> O <sub>5</sub>	< 0.01	Ni	5		
LOI	95.06	Hg	82		
Total	99.79	As	171		

confirm the high iron content. Notable are also the high concentrations of As, Sb, Hg, Mo, and Au in the cinders.

#### 4.2. Sulfur speciation in Cinder Pool

Cinder Pool was sampled on 24 and 26 August 1995, 20 August 1996, and 12 August 1997. Multiple samples were collected at different locations of the pool and at different depths for each set of analyses. The concentrations of thiosulfate, polythionate,

sulfate and H<sub>2</sub>S for all the samples are entered in Table 3. It is important to note that the amount of sulfur spherules was much lower in 1997 than either of the previous two years (see pictures available at <http://sbmp97.ess.sunysb.edu/>). In 1995, about 70% of the surface of the pool was covered with cinders; in 1996, the coverage was about 60%; while in 1997, not more than 5% of the surface was covered with cinders.

Thiosulfate concentrations obtained on 24 and 26 August 1995 were essentially the same. Thiosulfate

Table 3  
Sulfur compounds in Cinder Pool of Yellowstone National Park (μM)<sup>a</sup>

Date	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup>	N	H <sub>2</sub> S	SO <sub>4</sub> <sup>2-</sup>	Location in the pool
8/24/95	44.8	1.3	4.9	16	n.a.	Pool edge, cinder side, surface
8/24/95	45.4	7.8	4.4	16	1196	Pool edge, cinder side, surface
8/24/95	43.8	5.6	4.1	16	1168	Pool edge, no cinder side, surface
8/24/95	42.8	4.1	4.5	16	1150	Pool center, ~1.5 m deep
8/26/95	43.3	n.d.	–	48	1299	Pool center, ~3 m deep
8/26/95	43.5	n.d.	–	48	1240	Pool center, ~1 m deep
8/26/95	43.7	n.d.	–	48	1275	Pool center, ~10 cm deep
8/26/95	42.9	n.d.	–	48	1232	Pool edge, cinder side, ~10 cm deep
8/26/95	43.5	n.d.	–	48	1228	Pool edge, no cinder side, ~10 cm deep
8/26/95	43.3	11.0 <sup>b</sup>	–	n.a.	n.a.	Pool edge, cinder side, surface
8/20/96	37.3	8.9	4.8	30	n.a.	Pool edge, cinder side, surface
8/20/96	37.7	4.5	4.8	30	n.a.	Pool edge, no cinder side, surface
8/20/96	35.6	5.0	4.7	30	n.a.	Pool center, ~1.5 m deep
8/12/97	71.0	4 <sup>b</sup>	–	0.6	810	Pool edge, among cinders
8/12/97	70.0	5 <sup>b</sup>	–	0.6	815	Pool edge, no cinder

<sup>a</sup> Zinder and Brook (1977) reported a SO<sub>3</sub><sup>2-</sup> concentration of 1.5 μM, a H<sub>2</sub>S concentration of 0 μM, and 528 μM S(0). n.a.: not analyzed; n.d.: not detected.

<sup>b</sup> SCN<sup>-</sup> concentration, as shown in reaction (1), one SCN<sup>-</sup> forms for each S<sub>4</sub>O<sub>6</sub><sup>2-</sup> molecule converted and two SCN<sup>-</sup> form for each S<sub>5</sub>O<sub>6</sub><sup>2-</sup> converted. Because the water contains both S<sub>4</sub>O<sub>6</sub><sup>2-</sup> and S<sub>5</sub>O<sub>6</sub><sup>2-</sup>, the total polythionate concentration is expected to be between 0.5 [SCN<sup>-</sup>] and [SCN<sup>-</sup>].

concentrations measured on 20 August 1996 were, however, about 20% lower than those in 1995. Two samples collected in 1997 had much higher thiosulfate concentration than in any of the earlier samples (Table 3). The distribution of thiosulfate throughout the pool was rather uniform in all three sets of analyses. Polythionate concentrations were more variable than thiosulfate concentrations; both temporal and spatial variability was observed. On 24 August 1995, water sampled from the surficial layer of the pool covered with cinders had the highest polythionate concentration, while the water sampled from a depth of about 1.5 m was significantly lower in polythionate concentration. On 26 August 1995, when the  $\text{H}_2\text{S}$  concentration was three times higher than on 24 August 1995, polythionates were only detected in surficial water taken from among the cinders. Polythionate concentrations measured on 20 August 1996 were somewhat lower than those on 24 August 1995, but the same spatial variability was observed. The measured average length of sulfur chain of polythionate was 4.1–4.9, indicating that some higher polythionates ( $x > 4$ ) must have been present in addition to tetrathionate ( $\text{S}_4\text{O}_6^{2-}$ ). In 1997, the polythionate concentrations were uniformly low. It is furthermore important to note that the sulfate concentration in the two samples collected in 1997 was significantly lower than in the previous two years.

#### 4.3. Sulfur hydrolysis experiments

The concentrations of thiosulfate, sulfate, and sulfite are shown in Fig. 2 as a function of time for the sulfur hydrolysis experiments at temperatures of 120 and 150°C. Thiosulfate is clearly an intermediate product of the sulfur hydrolysis reaction under the experimental conditions. Thiosulfate concentrations in the experiments at 120 and 150°C reached a maximum after 2–3 days of reaction, then decreased gradually. For example, after 10 days of reaction in the experiment at 150°C, the thiosulfate concentration decreased to about 60% of its maximum value. By contrast, in the experiment at 120°C, the thiosulfate concentration remained at about 90% of the maximum concentration. The results indicate that sulfate becomes the predominant hydrolysis product as the temperature increases.  $\text{H}_2\text{S}$  was detected as a product of sulfur hydrolysis in all experiments. The  $\text{H}_2\text{S}$

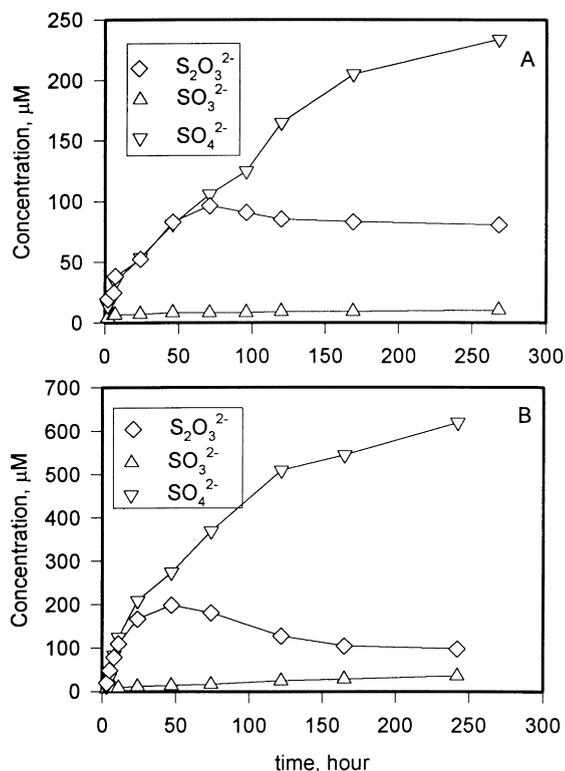


Fig. 2. Formation of thiosulfate, sulfate and sulfite from the hydrolysis of elemental sulfur at pH 4.0 and a temperature of: (A) 120°C; and (B) 150°C. The mass loading of sulfur is 0.8 g/800 ml solution.

concentrations, however, were not monitored in these experiments, since partitioning of  $\text{H}_2\text{S}$  in the vapor phase of reaction vessels (experiments at 120 and 150°C) and volatilization (experiment at 100°C) made it impossible to determine the stoichiometric relationship between  $\text{H}_2\text{S}$  and the sulfoxyanions.

At pH 6.0 and 8.0, thiosulfate was observed as the only sulfoxyanion in the sulfur hydrolysis at 100°C. The initial rate of thiosulfate follows a rate law of fractional order (0.52) with respect to pH (see Fig. 3):

$$\log R_{\text{thiosulfate}} = -11.36 + 0.52 \text{ pH} \quad (2)$$

where  $R$  is the thiosulfate formation rate in M/s. Fig. 4 shows the changes in pH, thiosulfate, sulfate and sulfite concentration for an experiment at 100°C in which the pH was allowed to drift from an initial pH of 8. Such a solution may be representative of the initial pH condition of deep hydrothermal water discharging into the bottom of Cinder Pool, as

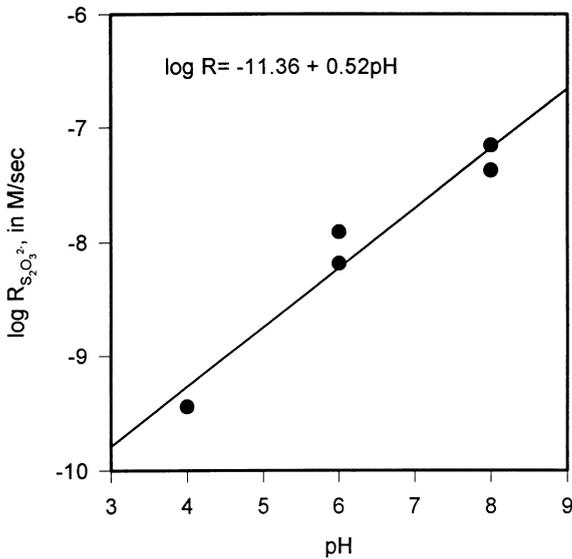


Fig. 3. The initial rate of thiosulfate formation as a function of pH for the sulfur hydrolysis experiments at 100°C and 1 atm.

indicated by its high  $\text{Cl}^-$  concentration (601 mg/l, see Table 1). In this experiment, the pH of the solution decreased rapidly from 8 to about 4 along with the rapid increase in thiosulfate concentration, indicating that sulfur hydrolysis also generates acidity.

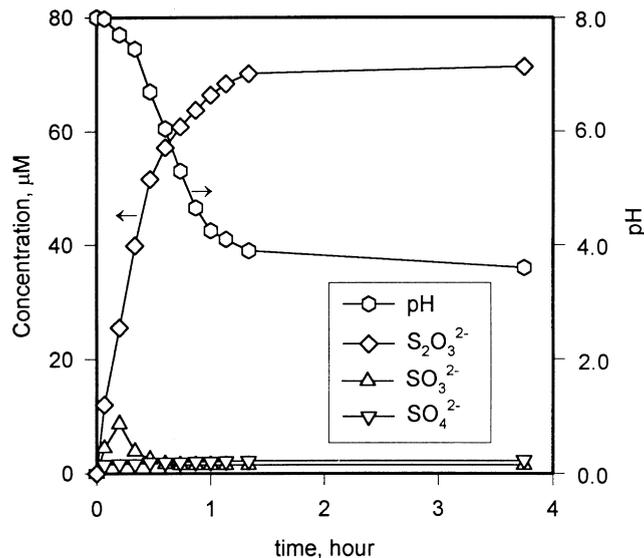
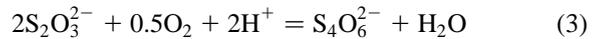


Fig. 4. Concentration of thiosulfate, sulfate, sulfite, and pH as a function of time for a free-drift sulfur hydrolysis experiment at 100°C. The initial pH was 8.0, while the initial sulfur/solution ration was 1 g/1000 ml.

#### 4.4. Cinder-catalyzed thiosulfate oxidation

Fig. 5A shows the decrease in thiosulfate concentration as well as consequential increase in total polythionates as a function of time at 90°C (polythionate concentration is here represented by the thiocyanate concentration generated by cyanolysis of the reacting solution, see reaction (1)). The 2:1 ratio of decomposed thiosulfate and generated thiocyanate concentration indicates that tetrathionate is the dominant oxidation product. Hence the reaction can be expressed as:



Initial tetrathionate formation rates obtained at 20, 50, and 90°C are summarized in Table 4 and Fig. 5B.

#### 4.5. Stability of polythionate in cinder pool

Results of the in situ polythionate decomposition experiment are shown in Fig. 6. When the water was separated from the sulfur spherules, polythionate decomposed at a rate of about 0.3  $\mu\text{M}/\text{min}$ . This implies a half life of about 0.5 h for polythionate in the absence of the sulfur spherules at the conditions in Cinder Pool.

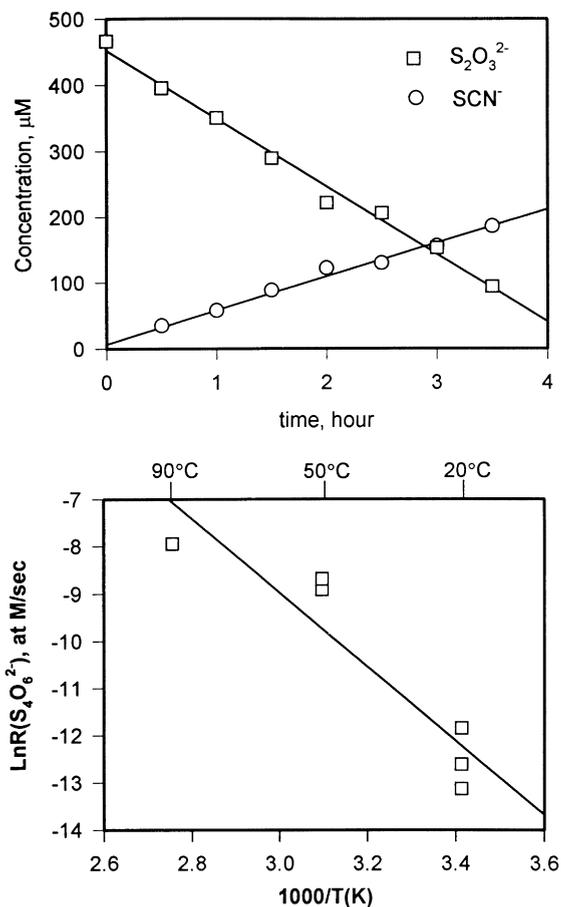


Fig. 5. The thiosulfate and thiocyanate concentration as a function of time from the thiosulfate oxidation in the presence of crushed sulfur spherules at 90°C, and a pH of 4.0 (A). Measured initial rate of thiosulfate formation as a function of temperature; note logarithmic scale for rate (B). Mass loading of crushed sulfur spherules equals 1.0 g/100 ml solution in all experiments.

Table 4

$S_4O_6^{2-}$  formation rate of the  $S_2O_3^{2-}$  oxidation in the presence of crushed sulfur spherules (1.0 g/100 ml), pH 4.0,  $[S_2O_3^{2-}]_0 = 0.5$  mM

$T$ (°C)	Rate ( $10^{-7}$ M/s)
20	0.03
20	0.01
20	0.01
50	0.67
50	0.54
90	1.43

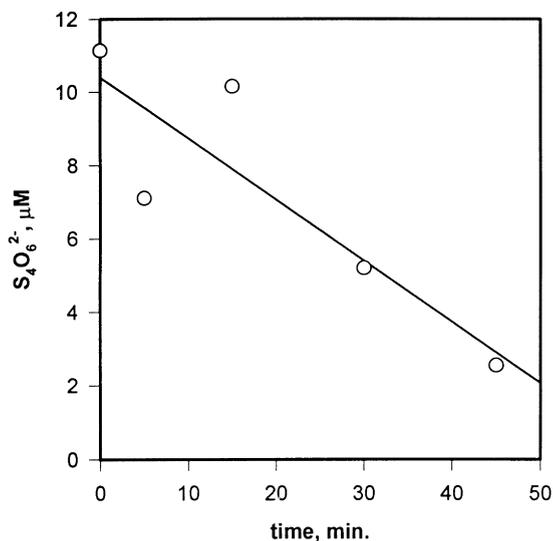


Fig. 6. The decomposition of polythionate in Cinder Pool on 26 August 1995. Samples were collected from the surficial layer of water covered with sulfur spherules. The water was separated from the spherules by filtration into a glass sample bottle. The sealed sample bottles were submerged back into the pool, and retrieved and analyzed at the desired time.

#### 4.6. Decomposition of polythionate by $H_2S$

The formation of thiosulfate from the aqueous interaction of tetrathionate and hydrogen sulfide were studied at pH 1 and 20°C. Fig. 7A shows thiosulfate concentrations as a function of time for selected experiments. Fig. 7B and Table 5 summarize the measured initial rate for all experiments. The experiments were carried out with three starting  $S_4O_6^{2-}$  solutions (labeled M, N, and P, respectively, in Table 5). Experiments M1, N1, and P1 were conducted immediately following the preparation of the  $S_4O_6^{2-}$  stock solutions. The other experiments were conducted with the same  $S_4O_6^{2-}$  solutions but at least 1 h after preparation of the stock solution. It is evident from Fig. 7 that the rates of thiosulfate formation for the first experiment (i.e. M1, N1, and P1) in all three sets of experiments are substantially lower than the rates obtained in the experiments started later with the same  $S_4O_6^{2-}$  solutions. The polythionate speciation in the  $S_4O_6^{2-}$  stock solution was monitored for several hours after preparation to examine if changes in polythionate speciation occur that may explain the difference in reactivity over time.

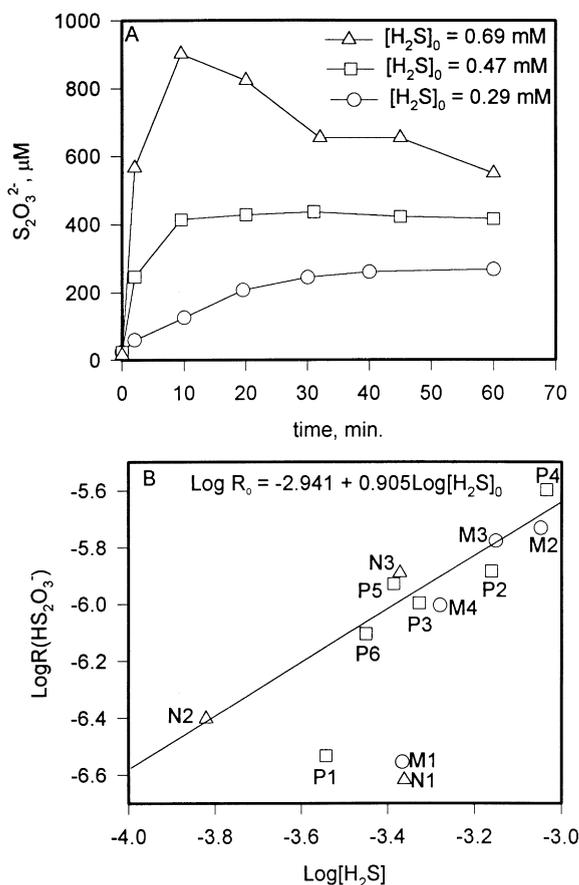


Fig. 7. (A) Thiosulfate concentration as a function of time for selected experiments of aqueous polythionate– $H_2S$  interaction at pH 1, 20°C. (B) Initial rate of thiosulfate formation as a function of initial  $H_2S$  concentrations. The initial polythionate concentration was about 0.5 mM for all the experiments. Note that the experiment were conducted from three starting solutions (labeled M, N, and P), and M1, N1, and P1 represent the first experiment of each series.

As shown in Fig. 8, the sodium tetrathionate used in this study was not the pure tetrathionate. Instead, it consists of about 90% tetrathionate, and 5% trithionate and 5% pentathionate. When this salt dissolves in 0.1 M HCl solution, the tetrathionate concentration decreases to about 70% of the nominal concentration, while both the trithionate and pentathionate concentration increase to about 15% of the nominal concentration after about 80 min. Within 2 h a steady state of polythionates speciation was reached which was maintained for at least 6 h.

The initial rates of thiosulfate formation obtained in

Table 5

Initial rate of  $S_2O_3^{2-}$  formation from aqueous  $S_4O_6^{2-}$ – $H_2S$  interaction at pH 1, 20°C

No.	$[S_4O_6^{2-}]_0$ ( $10^{-6}$ M)	$[H_2S]_0$ ( $10^{-6}$ M)	$R(S_2O_3^{2-})_0$ ( $10^{-6}$ M/s)
M1	519	432	0.278
M2	519	896	1.86
M3	519	706	1.67
M4	519	526	0.988
N1	496	439	0.293
N2	496	151	1.30
N3	496	286	1.01
P1	505	411	2.52
P2	505	690	1.17
P3	505	470	0.780
P4	505	924	0.240
P5	505	411	0.395
P6	505	356	1.28

these three sets of experiments (excluding M1, N1, and P1) indicate a rate law of first-order with respect to hydrogen sulfide:

$$\log R_{\text{thiosulphate}} = -2.941 + 0.905 \log[H_2S] \quad (4)$$

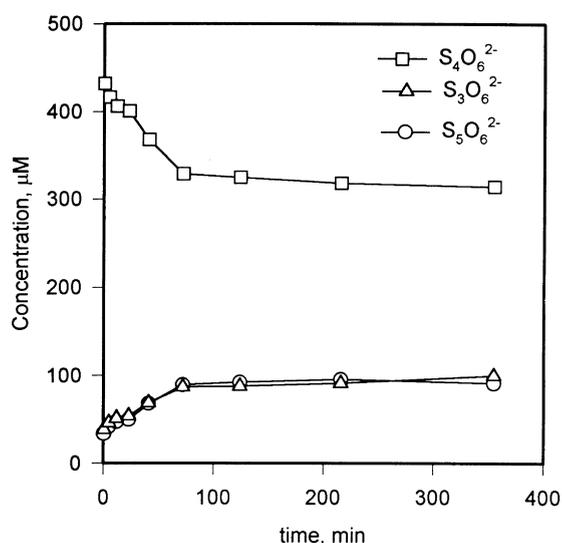


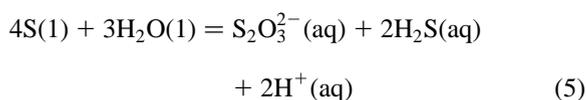
Fig. 8. Changes in polythionate speciation in 0.1 M HCl solution at 20°C. The initial solution consists of 90% tetrathionate, 5% trithionate and 5% pentathionate, respectively. A steady-state speciation, consisting of 70% tetrathionate, 15% trithionate and 15% pentathionate, was reached about 80 min after the preparation of the stock solution.

## 5. Discussion

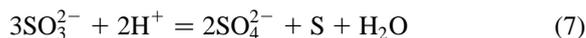
In the following sections, the mechanism of the formation and decomposition of thiosulfate and polythionate will be discussed separately.

### 5.1. Thiosulfate formation in Cinder Pool

The results show that thiosulfate is formed not only by sulfur hydrolysis in alkaline solutions as observed in early studies (Pryor, 1962; Giggenbach, 1974), but it is also formed during the initial stages of sulfur hydrolysis in acidic solutions. Hence, the initial step of sulfur hydrolysis in both alkaline and acidic solutions can be expressed as:



This suggests that the aqueous sulfur speciation formed during sulfur hydrolysis is controlled by the stability of thiosulfate, which is highly dependent on pH and temperature of the solution (Xu, 1997). Xu (1997) showed that at pH 4 and 150°C thiosulfate decomposes according to:

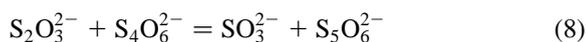


As seen in the sulfur hydrolysis experiments, thiosulfate is persistent at pH 4 up to 120°C (the temperature of the molten S layer in Cinder Pool). As temperature increases to 150°C, the concentration of thiosulfate falls (and the sulfate concentration increases), consistent with enhanced thiosulfate decomposition via reactions (6) and (7) (Xu, 1997). This suggests that if sulfur hydrolysis reactions were to take place at temperatures substantially higher than those observed at the bottom of Cinder Pool, the thiosulfate concentrations in the water are expected to be much lower than those observed in Cinder Pool. None of the springs in YNP sampled by Xu et al. (1998) with pH < 5 contained any significant amounts of thiosulfate except Cinder Pool. This is consistent with the fact that Cinder Pool is the only spring known to be underlain by a pool of molten sulfur with a temperature of about 120°C. If the waters of other acid sulfate chloride springs had interacted with sulfur within the

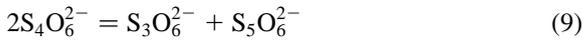
aquifers underlying Norris Geyser Basin, the prevailing high subsurface temperature in this basin (White et al., 1988) would restrict the occurrence of thiosulfate in any significant amount to near-neutral pH waters. In fact, among acid-sulfate-chloride springs sampled in Norris Geyser Basin, only Cistern Spring (pH 6.1) contains thiosulfate at a concentration higher than in Cinder Pool (Xu et al., 1998). Further investigations on Cistern Spring are underway.

### 5.2. Polythionate formation in cinder pool

The formation of polythionate in acidic crater lakes has been attributed to interactions between magmatic SO<sub>2</sub> and H<sub>2</sub>S gases (Takano, 1987; Takano et al., 1994a,b). In YNP, SO<sub>2</sub> gas has never been detected in any significant amount (Zinder and Brock, 1977). Furthermore, the low sulfate concentration in deep hydrothermal water contained in the zone closest to the underlying magma suggests that the flux of magmatic SO<sub>2</sub> into the hydrothermal system is limited. Low concentrations of sulfate in the deep system at Norris Geyser Basin has been known for some time (Schoen and Rye, 1970; Truesdell et al., 1978). While SO<sub>2</sub> is virtually absent, many fumarolic gases contain some H<sub>2</sub>S (Zinder and Brock, 1977), and the deepest hydrothermal waters in Norris Geyser Basin do contain hydrogen sulfide (Fournier et al., 1992). Because of the lack of SO<sub>2</sub> in the Norris system, the polythionate in Cinder Pool must form via a mechanism that does not require the presence of SO<sub>2</sub>. The experimental result of the thiosulfate oxidation experiment in the presence of the crushed sulfur spherules indicates that tetrathionate can be formed via reaction (3). This pathway has been studied in detail by Xu and Schoonen (1995). However, the measured average sulfur-chainlength of polythionate in Cinder Pool is 4.1–4.9, which indicates that a fraction of the polythionates has a chainlength longer than 4 S atoms. In experimental studies by Xu and Schoonen (1995), only tetrathionate is found. The difference in average chainlength between the experiment and samples taken from Cinder Pool may be the result of a slow reaction producing other polythionates. One possibility is a reaction between thiosulfate and tetrathionate forming pentathionate and sulfite:



Higher polythionate (i.e.  $n > 5$ ) can be generated via similar reactions (Lyons and Nickless, 1968). A second possible reaction is:



Reaction (9) does not change the average chainlength, but since trithionate was not measured in the field disproportionation of some tetrathionate via this reaction would raise the apparent chainlength of the polythionate mixture. Trithionate is not measured on a routine basis because it requires heating of the sample, which is impractical for on site analysis. The lack of higher polythionates in products of thiosulfate oxidation in the presence of pyrite (Xu and Schoonen, 1995) or sulfur spherules in the experiments reported here may reflect that on the time scale of the experiments the progress of reactions (8) and (9) is limited.

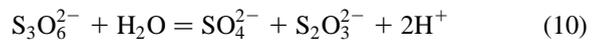
Polythionate formation via oxidation of thiosulfate catalyzed by pyrite dispersed in the sulfur spherules also explains the lack of polythionate in other acid-sulfate chloride springs and the close association of polythionate with the sulfur spherules. Xu et al. (1998) determined sulfur speciation in 39 hydrothermal features in YNP and found detectable polythionate in Cinder Pool only. While the type of water in Cinder Pool is found in several other springs in YNP, Cinder Pool is the only feature in which the prerequisite pyrite is present to catalyze oxidation of thiosulfate to tetrathionate. The significance of the pyrite-catalyzed thiosulfate oxidation is particularly well illustrated by the high thiosulfate concentration in the two samples collected in 1997. In 1997, cinders were largely absent, effectively reducing the availability of catalyst, and as a result the thiosulfate concentration was much higher than in either of the previous years when most of the surface of the pool was covered with cinders.

Sulfur spherules present in acid crater lakes appear to promote the formation of polythionates but it is not clear how important the pyrite-mediated mechanism is. Takano et al. (1994b) reported that polythionate concentrations of waters squeezed out of sulfur spherules were several orders of magnitude higher than  $S_xO_6^{2-}$  concentrations in lake water samples (Takano et al., 1994b). There are two possible causes for high polythionate concentrations in these waters. The sulfur spheres may have contained  $SO_2$  and  $H_2S$  gas

and the spherules may have acted as microreactors. In addition, polythionates may form via the oxidation of thiosulfate catalyzed by metal sulfides dispersed in the floating sulfur spherules. The significance of this latter contribution is difficult to evaluate. It depends on the rate of polythionate formation via this process compared with other pathways. The rate via the spherule-catalyzed pathway depends on the thiosulfate concentration and the availability of the catalyst (see Xu and Schoonen, 1995, for rate laws governing the kinetics of this reaction).

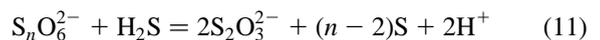
### 5.3. Decomposition of polythionate in Cinder Pool

Meyer and Ospina (1982) studied the decomposition of trithionate and tetrathionate in aqueous solutions with a starting pH of 4 and temperatures ranging from 50 to 70°C. They showed that decomposition of trithionate involves hydrolysis yielding sulfate and thiosulfate according to:



The initial step in the decomposition of tetrathionate is bimolecular disproportionation into trithionate and pentathionate according to reaction (9). The trithionate formed in reaction (9) can subsequently decompose via reaction (10). According to Meyer and Ospina (1982), thiosulfate acts as a catalyst in the initial step of tetrathionate decomposition. Extrapolating the rate data obtained by Meyer and Ospina to 90°C yields a half life of about 4 h. From the in situ polythionate decomposition experiment conducted in this study, a half life of 0.5 h at 90°C is obtained, eight times faster than the rate given by Meyer and Ospina (1982).

The decrease in polythionate concentration in Cinder Pool with increasing  $H_2S$  concentration suggests that a  $H_2S$ -mediated (or  $HS^-$ -mediated) decomposition is an important pathway of polythionate decomposition. The results of polythionate- $H_2S$  interaction experiments demonstrate that even in a solution of pH 1.0 at ambient temperature,  $H_2S$  can promptly degrade polythionate to thiosulfate. This result is consistent with experimental work summarized by Takano et al. (1994a). The overall reaction can be expressed as:



The experimental results showed that the reaction is faster for an aged polythionate solution than for a freshly prepared stock solution. The aged solution has a polythionate speciation containing relatively more pentathionate and trithionate than the freshly prepared solution. It is well known that trithionate cannot be degraded by nucleophilic species such as  $\text{CN}^-$  and  $\text{S(-II)}$  at room temperature (Lyons and Nickless, 1968). Hence, the increased reaction rate for the aged polythionate solution indicates a higher reactivity of pentathionate with  $\text{H}_2\text{S}$  than tetrathionate. It is important to note, however, that trithionate also may be decomposed by  $\text{H}_2\text{S}$  (or  $\text{HS}^-$ ) in hot solutions. This is expected because upon heating trithionate does react with  $\text{CN}^-$  (Kelly et al., 1969). Nevertheless, the experimental result indicates that  $\text{H}_2\text{S}$ -mediated decomposition of polythionate (i.e. reaction (11)) proceeds preferentially via reactions involving higher polythionates, while disproportionation (reactions (9) and (10)) proceeds preferentially via reactions with lower polythionates.

#### 5.4. Sulfur cycle in Cinder Pool

The results obtained in this study allow us to relate the formation and decomposition of thiosulfate and polythionate to the presence of sulfur spherules and molten sulfur in Cinder Pool. As shown schematically in Fig. 9, the major interactions between sulfur species in Cinder Pool can be summarized as follows:

(a) Sulfate,  $\text{H}_2\text{S}$ , and thiosulfate are generated by the hydrolysis of elemental sulfur by hydrothermal solution at the bottom of the pool (and in the shallow aquifer). Additional  $\text{H}_2\text{S}$  enters the pool as a gas phase, as indicated by the relatively constant thiosulfate concentration but highly variable  $\text{H}_2\text{S}$  concentration in Cinder Pool.

(b) At the surface of the pool, some thiosulfate is oxidized to tetrathionate by dissolved oxygen with the disseminated pyrite in the cinders as a catalyst. Tetrathionate interacts with thiosulfate producing higher polythionate.

(c) Polythionates decompose via interaction with  $\text{H}_2\text{S}$  to elemental sulfur and thiosulfate, and/or via the disproportionation-hydrolysis reaction to thiosulfate and sulfate.

(d) Thiosulfate disproportionates to elemental sulfur and sulfite; sulfite oxidizes rapidly to sulfate.

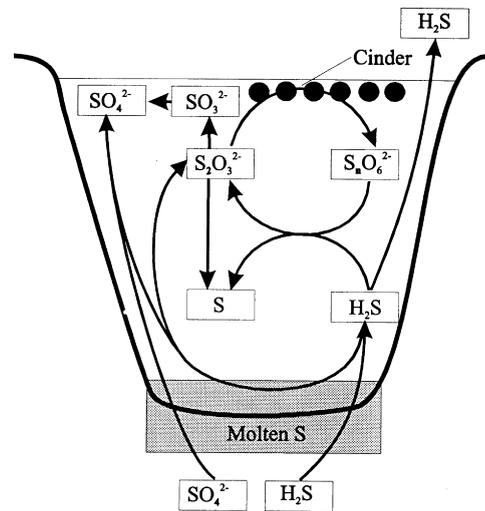


Fig. 9. Schematic diagram of inferred sulfur cycle of Cinder Pool in Norris Geyser Basin, Yellowstone National Park. The contributions of fluids and gases from depth are probably highly variable and contribute to the temporal variation in chemistry. Reactions between dissolved sulfur species are complex and only those processes are indicated that we think are most important in forming the unique sulfoxyanion speciation observed in this pool. See text for details.

It is important to note that without the molten sulfur pool no significant amount of thiosulfate or any sulfur spherules could be formed in Cinder Pool. Furthermore, without the sulfur spherules, no polythionates could be generated. The formation of thiosulfate and polythionates influences the normal pathway of  $\text{H}_2\text{S}$  oxidation in acid hydrothermal waters. Under acid conditions,  $\text{H}_2\text{S}$  oxidation by molecular oxygen is a slow process although its rate increases with temperature. Although of no importance in Cinder Pool due to the absence of dissolved ferric iron (Table 1), oxidation of  $\text{H}_2\text{S}$  in many acidic hot springs may proceed with ferric ions as oxidant. Sulfate is the main product of this reaction along with minor amounts of elemental sulfur or sulfite (Zinder and Brock, 1977). However, in the presence of polythionates, some  $\text{H}_2\text{S}$  is converted to elemental sulfur via reaction (11). The diversion of  $\text{H}_2\text{S}$  via reaction (11) limits the amount of sulfate formed and the amount of acid generated.

#### 5.5. Origin of sulfur in Cinder Pool

While the presence of the molten sulfur layer

underlying Cinder Pool appears to be the determining factor in the sulfur speciation of the water, it is not clear what the origin of the elemental sulfur is and why this type of hydrothermal feature is so rare. On the basis of sulfur isotopic compositions and chemical compositions of a large set of water samples from many hydrothermal features in Norris Geyser Basin, Fournier et al. (1998) have postulated that the composition of many waters in the area referred to as One Hundred Spring Plain, which includes Cinder Pool, is affected by interaction with sulfate-bearing minerals and/or elemental sulfur at temperatures between 180 and 220°C. Fournier et al. (1998) point out that sulfate-bearing minerals, such as alunite and jarosite, as well as elemental sulfur are common mineral constituents of solfataras, which are likely to have formed and been preserved in the Norris region (a suggestion also made by Donald White, oral communication). It is possible that Cinder Pool represents a situation in which the bottom of the pool has intersected a buried solfataras. All other features on the One Hundred Spring Plain appear to be shallow. Because the melting point of sulfur is around 120°C, a feature must be sufficiently deep in order to have temperatures at the bottom that could lead to liquefaction of elemental sulfur. However, if temperatures are much higher than 120°C, sulfur hydrolysis will yield predominantly sulfate and the viscosity of the sulfur will decrease to a point where gases are expected to pass through the liquid sulfur layer without forming spherules. Furthermore, the geometry of the feature must be such that there is sufficient residence time of the water to allow sulfur hydrolysis reactions to proceed. Perhaps the combined requirements of the presence of elemental sulfur (here presumably as a constituent of a solfataras), bottom temperatures near 120°C, and sufficient depth restrict the occurrence of features like Cinder Pool.

### 5.6. Implications to sulfur chemistry in acid crater lake

Although there are some profound differences in physico-chemical conditions between Cinder Pool and acid crater lakes hosted by active volcanoes (cf. Bennett and Raccichini, 1978; Francis et al., 1980; Oppenheimer and Stevenson, 1989; Hurst et al.,

1991; Takano et al., 1994a,b), this study provides some insight into the interactions of sulfur species in acid crater-lake environments.

First, thiosulfate is involved in both the formation and decomposition reactions of polythionate in Cinder Pool. The role of thiosulfate in crater-lake environments, however, has never been investigated systematically (see Takano et al., 1994a,b). Because of the high acidity of crater-lake waters, thiosulfate is expected to be at very low concentrations, but may still be an important intermediate in the formation and decomposition of polythionate. Webster (1987) and Xu et al. (1998) detected thiosulfate in springs of pH 2, and showed that the thiosulfate concentrations in acid springs are controlled by hydrolysis and disproportionation of elemental sulfur. Calculations show that in solutions with pH 1–2 one may expect thiosulfate concentrations in the low  $\mu\text{M}$  level if the sulfur hydrolysis reaction reaches equilibrium (the exact amount depends on the  $\text{H}_2\text{S}$  concentration, see Xu et al., 1998).

Second, drastic decreases in polythionate concentration, thought to be a good indicator for impending volcanic eruption, have been interpreted to be the result of an increase in  $\text{SO}_2/\text{H}_2\text{S}$  ratio of gases discharging into crater lakes (Takano, 1987). The results obtained in this study demonstrate, however, that the interaction with excess  $\text{H}_2\text{S}$  can also be an effective pathway for polythionate decomposition.

Third, because of the unstable nature of intermediate sulfur species, on site analyses for polythionates and thiosulfate is highly desirable. All the reported data concerning polythionate in acid crater lakes have been analyzed several days to several years after collection of the samples, which usually were not preserved. Although an underestimation of polythionate concentration is unlikely because polythionates are stable in acid water (Takano and Watanuki, 1988; Takano and Watanuki, 1990; Takano et al., 1994a), their concentration could be overestimated due to the formation of additional polythionates via oxidation of other intermediate sulfur species such as thiosulfate. In order to understand the mechanism of polythionate formation and decomposition in the acid crater lake environment, it is necessary to investigate the sulfur speciation on site, including not only polythionates but also other intermediates, especially thiosulfate.

## 6. Conclusions

The detailed on site study of aqueous sulfur speciation in Cinder Pool of YNP and the complementary laboratory experiments support the following conclusions:

(1) Thiosulfate is the immediate sulfoxyanion formed from the hydrolysis of elemental sulfur in both alkaline and acidic solution at elevated temperatures. Under the pH and temperature conditions of Cinder Pool, thiosulfate persists at significant concentrations. At higher temperature or lower pH, however, the decomposition of thiosulfate proceeds too fast to sustain significant concentrations.

(2) Polythionate in Cinder Pool is generated from the sulfur-spherules-catalyzed oxidation of thiosulfate. This reaction is probably catalyzed by pyrite dispersed in the spherules. The mechanism for this catalytic reaction has been worked out earlier (Xu and Schoonen, 1995).

(3) The polythionates in turn decompose to thiosulfate and sulfate via a disproportionation-hydrolysis pathway, and to thiosulfate and elemental sulfur via interaction with H<sub>2</sub>S.

(4) The cycling of sulfur between polythionate and thiosulfate leads effectively to the oxidation of some H<sub>2</sub>S to elemental sulfur rather than sulfate.

## Acknowledgements

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