Sulfur redox chemistry and the origin of thiosulfate in hydrothermal waters of Yellowstone National Park

D.K. Nordstrom, K.M. Cunningham & J.W. Ball
US Geological Survey, Water Resources Division, Boulder, Colo., USA

Y. Xu & M.A.A. Schoonen
Department of Geosciences, SUNY at Stony Brook, N.Y., USA

ABSTRACT: Thiosulfate ($S_2O_3^{2-}$), polythionate ($S_xO_6^{2-}$), dissolved sulfide (H_2S), and sulfate (SO_4^{2-}) concentrations in 39 alkaline and acidic springs in Yellowstone National Park were determined. The analyses were conducted *on site*, using ion chromatography for thiosulfate, polythionate, and sulfate, and using colorimetry for dissolved sulfide. Thiosulfate concentrations ranged from <0.01 to 8 ppm. Polythionate was detected only in Cinder Pool, Norris Geyser basin, at concentrations up to 1.8 ppm, with an average sulfur-chain-length from 4.1 to 4.9 sulfur atoms. The results indicate that no thiosulfate occurs in the deeper parts of the hydrothermal system. Thiosulfate may form from (1) hydrolysis of native sulfur by hydrothermal solutions in the shallower parts (<50 m) of the system, (2) oxidation of dissolved sulfide upon mixing of a deep hydrothermal water with aerated shallow groundwater, and (3) the oxidation of dissolved sulfide by air. Air oxidation of H_2S-containing hot springs proceeds very rapidly.

1. INTRODUCTION

The occurrence of thiosulfate in hydrothermal waters has been investigated for many active hydrothermal systems throughout the world (e.g., Allen and Day, 1935; Boulegue, 1978; Ivanov, 1982; Subzhiyeva and Volkov, 1982; Webster, 1987; Veldeman et al., 1991; Migdisov et al., 1992). The interest in thiosulfate in hydrothermal solutions stems from the notion that thiosulfate may be of importance as a complexer of precious metals, and as an intermediate in sulfur isotope exchange between sulfate and dissolved sulfide.

As shown in laboratory studies, thiosulfate may easily form as a result of incomplete oxidation of dissolved sulfide (defined operationally as that measured using the methylene blue colorimetric method and includes H_2S, HS^-, and S_x^{2-}; e.g., Chen and Morris, 1972; O'Brien and Birkner, 1977; Zhang and Millero, 1993). Therefore, it is not clear whether the thiosulfate detected in surficial hot waters is representative of deep hydrothermal solutions. Furthermore, sampling and preservation may significantly affect sulfur speciation in hot spring waters between the time of sampling and analysis. Oxidation of dissolved sulfide species to thiosulfate occurs rapidly upon brief exposure to oxygen and thiosulfate decomposes slowly over longer periods of time. Consequently, thiosulfate concentrations reported for hydrothermal waters will be affected by changes after sampling.

As part of a comprehensive investigation into the geochemistry of intermediate sulfoxyanions in hydrothermal solutions, the goal of this study is to evaluate the abundance and origin of thiosulfate in surficial hydrothermal waters in Yellowstone National Park (YNP). To minimize the formation or decomposition of thiosulfate after sampling, the analyses were conducted *on site* in a mobile laboratory operated and maintained by the U.S. Geological Survey. Detailed studies were conducted at Azure Spring and Ojo Caliente Spring in Lower Geyser Basin, Cinder Pool in Norris Geyser Basin, Angel Terrace Spring of Mammoth Hot Springs, and Frying Pan Spring located near Norris Geyser Basin.

2. SAMPLING AND ANALYSES

Sampling and analyzing waters containing thiosulfate and polythionates is challenging. The storage time was kept as short as practically possible by analyzing the samples on site. For small and non-violent springs, waters were drawn into a 60 mL plastic syringe through Teflon tubing (0.31 cm ID). The sample was immediately filtered using a syringe

filter (0.45 mm) and collected in a 30 mL sampling bottle. For large and violent features, samples were collected using a stainless steel thermos can attached to an aluminum pole. Samples for thiosulfate determination were collected in a 30 mL amber glass bottle containing 1mL of a 1M $ZnCl_2$ solution. The bottles were filled to the rim in order to avoid trapping atmospheric oxygen. The bottles were kept on ice until analysis. For analysis, an aliquot of water was drawn into a 3 mL syringe and injected into a Dionex 2010i/2000i ion chromatograph through a luer-lock syringe filter (0.45 mm pore-size). Using two AG4A guard columns in series, in combination with a standard $NaHCO_3/Na_2CO_3$ eluent, it was possible to determine thiosulfate within 3 minutes. Using a conductivity detector, the detection limit for thiosulfate is 0.01 ppm. Samples for polythionate analysis were collected in 30 mL amber glass bottles containing 1mL of 1M $ZnCl_2$, 1mL of 1M NaOH, and 1mL of 1M KCN solutions. Polythionate concentrations and average chain lengths were determined using alkaline cyanolysis modified from a method by Kelley et al. (1969), Moses et al. (1984), and Schoonen (1989). The detection limit of thiocyanate was 0.05 ppm, and the retention time is about 6 minutes.

Concentrations of dissolved sulfide were determined on site using a portable HACH DR-2000 UV-Vis absorption spectrometer. The HACH method # 8131, based on the methylene blue method, was used. The detection range is 0.666 - 0.001 ppm, and some samples had to be diluted. Dissolved oxygen was measured using the Winkler method, the fixed samples were titrated typically within 2 hours of collection.

3. RESULTS AND CONCLUSIONS

The $S_2O_3^{2-}$, $S_nO_6^{2-}$, H_2S and SO_4^{2-} concentrations for 6 selected hot springs of YNP are given in Table 1.

Ojo Caliente, representative for low-thiosulfate and high-sulfide springs, was studied in detail. Ojo Caliente consists of a pool and a well-defined drainage system (photos of this spring and others studied in detail are accessible via the WWW, *http://sbmp97.ess.sunysb.edu/*). The water in the pool contains 1 ppm sulfide, but only 0.27 ppm thiosulfate and 0.1 ppm dissolved oxygen. As the water discharges into the drainage, the dissolved oxygen content increases rapidly (Fig. 1A). As a result, sulfide is oxidized to thiosulfate and sulfate. Sulfide decreases at an average rate of about 0.05 ppm s^{-1}, while thiosulfate forms at an average rate of 0.01 ppm s^{-1}. Sulfate increases at a rate about 0.02 ppm s^{-1} after an initial lag period, suggesting that sulfate is not the initial product of the oxidation of sulfide. It is important to note that only 25% of the discharged dissolved sulfide was oxidized to thiosulfate and sulfate, the remainder volatilizes to the atmosphere.

Rapid formation of thiosulfate from air oxidation of dissolved H_2S is illustrated by the results from Angel Terrace. In the orifice of this spring, the thiosulfate is below the detection limit (<0.01ppm), yet within 1 m of the orifice ($\leq$ 1 second travel time down a waterfall), the thiosulfate concentration increased to 0.5 ppm along with a rapid increase of dissolved oxygen concentration (see Fig. 1B).

Azure Spring is a hot spring which discharges alkaline bicarbonate-chloride water at a maximum flow rate of 2L/sec. Temperature fluctuating between 60° to 87°C have been observed. Fig. 2 shows changes in thiosulfate and dissolved sulfide concentrations along the drainage of Azure Spring. In contrast to the drainage profiles of Ojo Caliente and Angel Terrace, oxidation of dissolved sulfide after discharge does not contribute much to the thiosulfate concentrations along the Azure drainage. Instead, thiosulfate concentrations decreased slightly along the drainage. Notice that H_2S is much lower

Table 1. Sulfur species, chloride, and dissolved oxygen in selected hot springs.

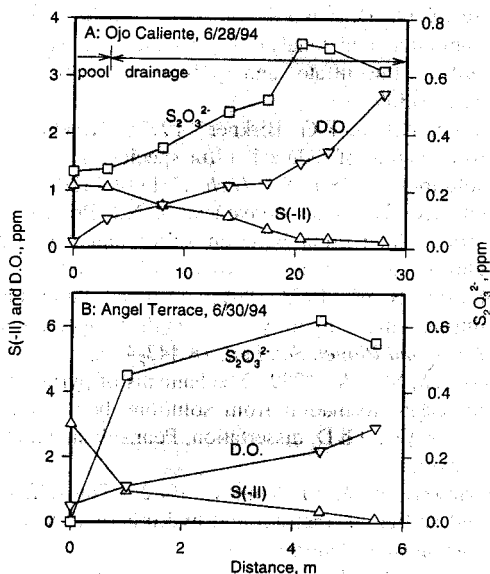| Spring	T °C	pH	D.O. ppm	$S_2O_3^{2-}$ ppm	$S_nO_6^{2-}$ ppm	H_2S ppm	SO_4^{2-} ppm	Cl ppm
Ojo Caliente Spring	93.0	7.8	0.1	0.27	NA.	1.09	20.7	324
Azure Spring	84.2	8.7	0.0	6.20	NA.	0.36	41.0	306
Cinder Pool	92.0	4.22	0.5	4.20	1.8	1.60	96.0	601
Cistern Spring		6.10		7.93	<0.05		89.5	431
Frying Pan Spring	78.2	2.34	2.4	0.63	<0.05	1.03	437	9
Angel Terrace Spring	72.2	6.43	0.5	<0.01	<0.05	3.01	547	165

NA: data not analyzed.

Figure 1. Concentration of sulfur in the form of thiosulfate, dissolved sulfide and dissolved oxygen vs distance along the drainage of (Fig. 1A) Ojo Caliente and (Fig. 1B) Angel Terrace Spring.
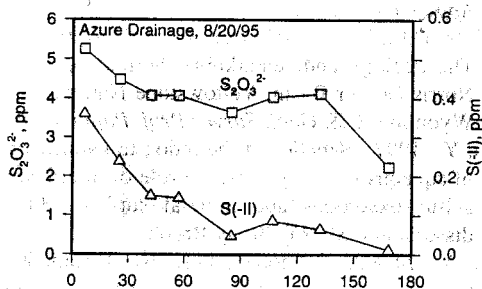

Figure 2. Thiosulfate and sulfide concentrations with distance along the drainage of Azure Spring.

and $S_2O_3^{2-}$ much higher at Azure than at Ojo Caliente or Angel Terrace.

The highest thiosulfate concentration (8 ppm) of all springs sampled in this study was obtained in Cistern Spring, a slightly acidic (pH 6.1) sulfate-chloride spring. The only sulfate-chloride spring with pH<5 that contains a significant amount of thiosulfate is Cinder Pool. Polythionate was found only in Cinder Pool. The concentrations varied from below detection (0.05 ppm) to 1.8 ppm. The average length of the sulfur chain of the polythionate was 4.1

to 4.9. Since Cinder Pool has not only a unique speciation of aqueous sulfoxyanions, but also contained floating sulfur spherules and a subsurface molten sulfur layer (White et al., 1988). Additional laboratory experiments were conducted to investigate the effects of the presence of the molten sulfur pool and sulfur spherules on the aqueous sulfur speciation. The experiments demonstrated that thiosulfate was readily generated from the hydrolysis of elemental sulfur at the conditions found at the bottom of Cinder Pool (120°C, pH 4). Furthermore, the polythionate in Cinder Pool appears to be formed by air oxidation of thiosulfate catalyzed by pyrite in the sulfur spherules.

The enrichment of thiosulfate in slightly acidic to alkaline chloride waters which are enriched in sulfate suggests that thiosulfate formation is part of the processes that lead to the formation of acidic sulfate-chloride waters. In laboratory experiments, thiosulfate has been observed to be an intermediate product in: 1) H_2S oxidation by dissolved oxygen (O'Brien and Birkner, 1977; Zhang and Millero, 1993); 2) H_2S - SO_3^{2-} interaction in aqueous solutions (Zhang and Millero, 1993; Xu et al., 1997); and 3) hydrolysis of elemental sulfur at elevated temperature (Robinson, 1973; Giggenbach 1974a, 1974b; Rafal'sky et al., 1983; Dadze and Sorokin, 1993; Xu et al., 1997). Each of these processes will be briefly discussed.

The fact that many springs have no significant amount of thiosulfate in their orifice or pools despite high dissolved sulfide concentration in some of these springs indicates that the aeration of dissolved sulfide in hot springs before discharging at the surface is not an effective mechanism for thiosulfate formation. While thiosulfate formation via oxidation of sulfide is of importance in the drainages, it plays little or no significant role in the springs and pools where the water first emerges.

There is little evidence to support a significant discharge of magmatic SO_2 gas into the hydrothermal system at YNP (Zinder and Brock, 1977).

One process which could result in local enrichment of thiosulfate in hydrothermal waters is the hydrolysis of elemental sulfur by ascending hydrothermal solutions. It is well known that in aqueous solutions at elevated temperatures, S_k opens and disproportionation reactions occur to form sulfide and sulfoxyanions (Dadze and Sorokin, 1993; Xu, 1997). The composition of the oxyanions

formed during the disproportionation depends on the temperature and pH of the solution.

Sulfur hydrolysis as the predominant source for thiosulfate in Norris Geyser Basin is consistent with the geochemical and sulfur-isotopic characteristics of waters in the hydrothermal system at Norris. When the ascending neutral hydrothermal solution comes in contact with locally buried sulfur deposits at shallow depth in Norris Basin, the hydrolysis of elemental sulfur can produce H_2S and thiosulfate.

REFERENCES

Allen, E.T. & A. Day 1935. Hot Springs of the Yellowstone National Park, Carnegie Institute of Washington, Pub. 466, 525 pp.

Boulegue, J. 1978. Metastable sulfur species and trace metals (Mn, Fe, Cu, Zn, Cd, Pb) in hot brines from the French Dogger. Am. J. Sci. 278:1394-1411.

Chen, K.Y. & J.C. Morris 1972. Kinetics of oxidation of aqueous sulfide by O_2. Environ. Sci. Tech. 6:529-537.

Dadze, T.P. & V.I. Sorokin 1993. Experimental determination of the concentrations of H_2S, HSO_4, $SO_{2(aq)}$, $H_2S_2O_3$, $S^0_{(aq)}$, and S_{tot} in the aqueous phase in the $S-H_2O$ system at elevated temperatures. Geochemistry International 30:36-51.

Giggenbach, W.F. 1974a. Equilibria involving polysulfide ions in aqueous sulfide solutions up to 240 °C. Inorganic Chem. 13:1724-17303.

Giggenbach, W.F. 1974b. Kinetics of the polysulfide-thiosulfate disproportionation up to 240 °C. Inorganic Chem. 13:1731-1734.

Ivanov, B.V. 1982. Recent hydrothermal activity in the region of the Karym group of volcanos. In: Hydrothermal mineral-forming solutions in the areas of active volcanism, ed. Naboka S. I., 39-48, Nauka Publisher, Novosibirsk.

Kelley, D.P. L.A. Chambers & P.A. Trudinger 1969. Cyanolysis and spectrophotometric estimation of trithionate in mixtures with thiosulfate and tetrathionate. Anal. Chem. 41:891-901.

Migdisov, A. A., T.P. Dadze & L.A. Gerasimovskaya 1992. Forms of sulfur in the ore-bearing hydrothermal solutions of Uzon Caldera (Kamchatka). Geochem. Inter. 29:17-27.

Moses, C.O., D.K. Nordstrom & A.L. Mills 1984. Sampling and analyzing mixtures of sulfate, sulfite, thiosulfate and polythionate. Talanta. 31:331-339.

O'Brien, D.J. & F.G. Birkner 1977. Kinetics of oxygenation of reduced sulfur species in aqueous solutions. Environ. Sci. Tech. 11:1114-1120.

Rafal'skiy, R.P., N.I. Medvedeva & N.I. Prisyagina 1983. Interaction between sulfur and water at elevated temperatures. Geokhimia 5:665-676.

Robinson, B. W. 1973. Sulfur isotope equilibrium during sulfur hydrolysis at high temperatures. Earth and Planet. Sci. Lett. 18:443-450.

Schoonen, M.A.A. 1989. Mechanisms of pyrite and marcasite formation from solutions between 25 and 300°C. Ph.D. dissertation, Pennsylvania State University.

Subzhiyeva, T. & I.I. Volkov 1982. Thiosulfates and sulfites in thermal and hydrothermal waters. Geochemical International 19:94-98.

Veldeman, E., L. Van't Dac, R. Gijbels & E. Pentcheva 1991. Sulfur species and associated trace elements in south-west Bulgarian thermal waters. Appl. Geochem. 6:49-62.

Webster, J.G. 1987. Thiosulfate in surficial geothermal waters, North Island, New Zealand. Appl. Geochem. 2:579-584.

White, D.E., R.A. Hutchinson &T.E.C. Keith 1988. The geology and remarkable thermal activity of Norris Geyser Basin, Yellowstone National Park, Wyoming. U.S. Geol. Survey Prof. Paper 1456.

Xu, Y. 1997. Kinetics of the redox transformations of aqueous sulfur species: the role of intermediate sulfur oxyanions and mineral surfaces, Ph. D dissertation, SUNY, Stony Brook

Xu, Y., M.A.A. Schoonen, D.K. Nordstrom, K.M. Cunningham & J.W. Ball 1997. Sulfur Geochemistry of Hydrothermal Waters in Yellowstone National Park: II The geochemical cycle of sulfur in Cinder Pool, in review.

Zhang, J.Z. & F.J. Millero 1993. Kinetics of oxidation of hydrogen sulfide in natural waters. In Environmental geochemistry of sulfide oxidation. ed C.A. Alpers & D.W. Blowes. 393-40., Am. Chem. Soc. Symp. Series 550, Washington, D.C.

Zinder, S. & T.D. Brock 1977. Sulfur dioxide in geothermal waters and gases. Geochim. Cosmochim. Acta 41:73-79.