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Sulfur geochemistry of hydrothermal waters in Yellowstone National Park: I. The origin of thiosulfate in hot spring waters

Y. Xu,[1] M. A. A. Schoonen,[1,*] D. K. Nordstrom,[2] K. M. Cunningham,[2] and J. W. Ball[2]

[1]Department of Geosciences, SUNY at Stony Brook, Stony Brook, New York 11794-2100, USA
[2]U.S. Geological Survey, Water Resources Division, 3215 Marine Street, Boulder, Colorado, 80303-1066, USA

Abstract—Thiosulfate ($S_2O_3^{2-}$), polythionate ($S_xO_6^{2-}$), dissolved sulfide (H_2S), and sulfate (SO_4^{2-}) concentrations in thirty-nine alkaline and acidic springs in Yellowstone National Park (YNP) were determined. The analyses were conducted on site, using ion chromatography for thiosulfate, polythionate, and sulfate, and using colorimetry for dissolved sulfide. Thiosulfate was detected at concentrations typically less than 2 μmol/L in neutral and alkaline chloride springs with low sulfate concentrations ($Cl^-/SO_4^{2-} > 25$). The thiosulfate concentration levels are about one to two orders of magnitude lower than the concentration of dissolved sulfide in these springs. In most acid sulfate and acid sulfate-chloride springs ($Cl^-/SO_4^{2-} < 10$), thiosulfate concentrations were also typically lower than 2 μmol/L. However, in some chloride springs enriched with sulfate (Cl^-/SO_4^{2-} between 10 to 25), thiosulfate was found at concentrations ranging from 9 to 95 μmol/L, higher than the concentrations of dissolved sulfide in these waters. Polythionate was detected only in Cinder Pool, Norris Geyser basin, at concentrations up to 8 μmol/L, with an average S-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, however, 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 dissolved oxygen upon discharge of the hot spring. Upon discharge of a sulfide-containing hydrothermal water, oxidation proceeds rapidly as atmospheric oxygen enters the water. The transfer of oxygen is particularly effective if the hydrothermal discharge is turbulent and has a large surface area. *Copyright © 1998 Elsevier Science Ltd*

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; Gundlach, 1965; 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 metals in the formation of ore deposits, including Au, Ag, and Pt-group ore deposits (Granger and Warren, 1969; Lakin et al., 1974; Baranova and Ryzhenko, 1981; Webster and Mann, 1984; Webster, 1986; Plimer and Williams, 1987; Benedetti and Boulegue, 1991; Anthony and Williams, 1994), and as an intermediate in sulfur isotope exchange between sulfate and dissolved sulfide (Ohmoto and Lasaga, 1982; Uyama et al., 1985; Spirakis, 1991). Compounds of Cu, Fe, Pb, and Zn with thiosulfate and other intermediate sulfoxyanions have been identified in Au deposits and carbonate-hosted Pb-Zn deposits, indicating the potential significance of thiosulfate and other intermediate sulfoxyanions in the genesis of these deposits (Spirakis, 1986; Kucha, 1988; Kucha et al., 1989, 1995; Kucha and Viaene, 1993). Furthermore, microbiologists have recognized the role of thiosulfate in the microbiologically mediated cycling of sulfur in natural waters (Jørgensen, 1990; Elsgaard and Jørgensen, 1992).

The role of thiosulfate in hydrothermal processes remains a subject of some controversy because its origin, stability, and activity in hydrothermal solutions is poorly understood. A major difficulty in evaluating the possible importance of thiosulfate in hydrothermal processes is the fact that all reported thiosulfate contents of hydrothermal solutions are based on analyses of surficial discharges of hot springs. As shown in laboratory studies (e.g., Chen and Morris, 1972; O'Brien and Birkner, 1977; Zhang and Millero, 1993), thiosulfate may easily form as a result of incomplete oxidation of dissolved sulfide (defined operationally as that measured using the methylene blue colorimetric method, this includes H_2S, HS^-, and S_x^{2-}). Therefore, it is not clear whether the thiosulfate detected in surficial hot waters is representative of deep hydrothermal solutions. Furthermore, sampling and preservation techniques 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 (seconds to minutes) to oxygen and thiosulfate decomposes slowly over longer periods of time (days). 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

*Author to whom correspondence should be addressed (mschoonen@notes.cc.sunysb.edu).

by the U.S. Geological Survey. The YNP was chosen as the study area not only because it is a unique natural laboratory of hydrothermal processes with manifestations of unparalleled diversity and intensity, but also because the road system within the YNP makes it possible to park the mobile laboratory vehicle close to features of interest. Furthermore, prior work by Allen and Day (1935) had reported thiosulfate in hot springs of the YNP.

Attempts to measure thiosulfate and polythionates in mineral waters and hot springs have been few. Clarke (1916) reports an analysis containing thiosulfate from a sulfide-rich spring in the eastern Pyrenees dating back to 1887. The determination of thiosulfate at Doughty Springs, Colorado, USA, was reported near the turn of the century (Headden, 1905). One of the first reports on the determination of intermediate sulfoxyanions in geothermal waters was that of Maclaurin (1911) who found pentathionate in the acid crater lake of White Island, New Zealand. Pentathionate was also found in salt encrustations of geothermal waters at Lassen National Park, California, USA, by Day and Allen (1925). Day and Allen (1925) found thiosulfate in the Geysers geothermal springs, California, USA, as well as at the YNP. Since Allen and Day (1935), there has been little work on the thiosulfate concentrations in the YNP waters. However, in the last three decades the geochemistry of the YNP hydrothermal system has been extensively investigated and a wealth of data is available to help understand the sulfur geochemistry in this hydrothermal system.

In this study, thirty-nine hot springs in six geyser basins or areas of the YNP were sampled. These springs range in chemical composition from alkaline chloride waters to acid sulfate waters. 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. In Azure Spring, an intermittent alkaline chloride spring with a well-developed 180 m long drainage, thiosulfate was detected at concentrations higher than dissolved sulfide. Azure Spring and its drainage were sampled repeatedly to evaluate the temporal change in thiosulfate concentration, the correlation with other aqueous sulfur species, as well as the changes in sulfur speciation along the drainage. Ojo Caliente Spring and Angel Terrace Spring represent examples of alkaline springs which are high in sulfide, but low in thiosulfate in their initial discharge. Cinder Pool is an acid sulfate-chloride hot spring with its surface partially covered by hollow black sulfur spherules and with a molten sulfur layer underlying the pool at 18 m depth. Not only thiosulfate but also polythionate were detected in significant amounts in this spring. Because of the peculiar physical features and the unique speciation of aqueous sulfur species of Cinder Pool, laboratory experiments were conducted to investigate the relationship between aqueous sulfur speciation and the sulfur spherules and molten sulfur. The result of these experiments, along with a detailed study of the sulfur speciation of this spring, will be reported in a separate publication (Xu et al., 1998). The complete analyses (major, minor, and trace elements) of these springs will also be reported in a separate communication. Details on the sampling, preservation and analyses of sulfur species in sulfide-bearing waters can be found in Cunningham et al. (1996) and elsewhere (M. A. A. Schoonen et al., written commun., 1997).

2. GEOCHEMICAL FRAMEWORK OF THE YNP HYDROTHERMAL SYSTEM

Since the late 1800s, the hydrothermal system of the YNP has been extensively studied. Chemical analysis of waters (mostly surficial samples) have been reported by Gooch and Whitfield (1888), Allen and Day (1935), Rowe et al. (1973), Thompson et al. (1975), Truesdell et al. (1978), Fournier (1979), Thompson and Yadav (1979), Mazor and Thompson (1982), Truesdell and Kennedy (1986), Kennedy et al. (1987), White et al. (1988), Fournier (1989), Sheppard et al. (1992), Fournier et al. (1992), Mariner et al. (1992), and Thompson and DeMonge (1996). The stable isotope geochemistry of the YNP waters has been studied to constrain the origin of various types of waters (Mariner et al., 1992; Truesdell et al., 1978; Fournier et al., 1998) and to delineate the areas that recharge the YNP hydrothermal system (Rye and Truesdell, 1992, 1993). Geological and geophysical studies include those by White et al. (1971), White et al. (1975), Smith and Christiansen (1980), Christiansen (1984), Fournier and Pitt (1985), White et al. (1988), and Smith and Braile (1994). In this section, the geochemical characteristics of the YNP hydrothermal waters are briefly reviewed to provide a framework for the interpretation of the formation of thiosulfate in the YNP waters.

The YNP is situated on a high volcanic plateau that consists of predominantly rhyolitic lavas and tuffs dated from 2.2 Myr to 0.6 Myr (Christiansen, 1984). Caldera ring fractures formed at about 2.0, 1.3, and 0.6 Myr are the dominant structures in this region (see Fig. 1). Along with a variety of geophysical anomalies, most of the hydrothermal manifestations are contained within the 0.6 Myr caldera, with activity concentrated along the edge of the main ring fracture and at the margins of the two resurgent domes. In addition, intensive hydrothermal activities occur in a N-S fault zone from Norris Geyser Basin northward to Mammoth Hot Springs. Most of the hydrothermal activity in the western half of the YNP, including all major geyser basins, is characterized by boiling springs that discharge significant quantities of neutral to slightly alkaline water rich in chloride and SiO_2. In the eastern part of the YNP, where most of the caldera is filled with relatively impermeable ash-flow tuff, vapor-dominated conditions are prevalent and the hydrothermal manifestations are typically in the form of fumaroles, mud pools, and acid-sulfate springs with little discharge (White et al., 1971). A general geochemical model of the YNP geothermal system has been presented by Truesdell and Fournier (1976), Truesdell et al. (1977), and Fournier (1989). The key hypothesis in this model is that all the water types identified in the YNP are related to a single deep "parent" water. This parent water is thought to evolve as cold water, recharging the hydrothermal system from the mountains to the north and northwest (Rye and Truesdell 1992, 1993), is heated to a temperature of about 350°C either within the caldera (Fournier, 1989) or beneath Roaring Mountain within the Norris-Mammoth corridor (White et al., 1988). The parent water contains about 440 ppm chloride and is presumably rich in volatiles such as CO_2 and H_2S, but contains little sulfate and bicarbonate (Truesdell et al., 1978; Fournier, 1989). The operation of subsurface physical and chemical processes (e.g., gas-water-rock interaction, boiling, mixing, and dilution) en route from the deep parent water to local reservoirs that feed hot springs and gey-
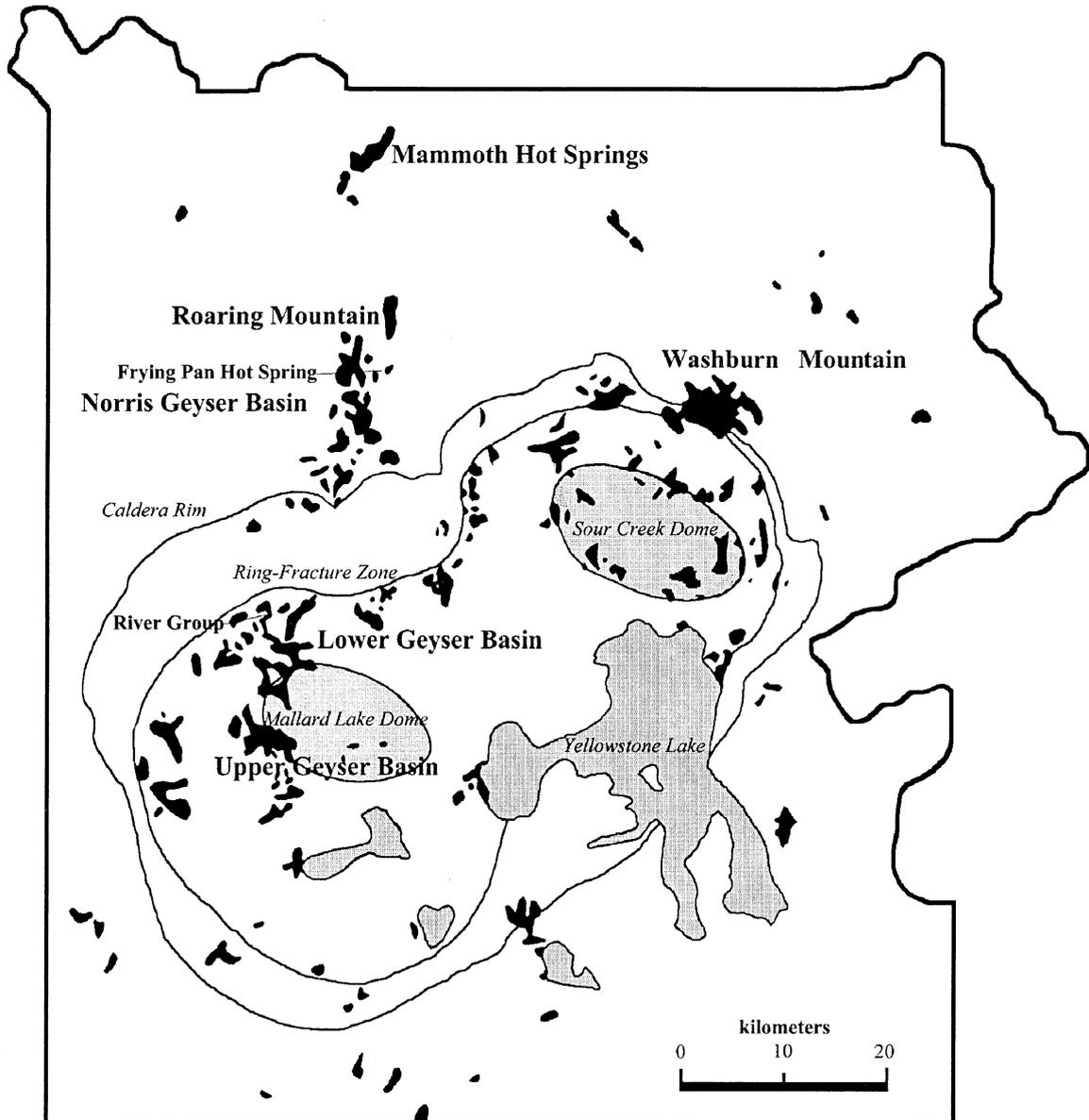
Fig. 1. Index map of Yellowstone National Park (YNP) showing 0.6 Myr caldera rim, the ring-fracture zone, resurgent domes, and major geyser basins and hydrothermal active areas investigated in this study. (adapted from White et al., 1988).

sers leads to the diversity in the chemistry of surficial hydro-thermal waters.

Geochemical characteristics of some chloride waters and sulfate-chloride waters sampled in this study in comparison with the parent water are shown in Fig. 2. Acid-sulfate springs were not included in Fig. 2 because most of the constituents of acid sulfate water originate from near surface leaching of country rocks (White et al., 1971). The waters discharged at Upper and Lower Geyser Basins are generally characterized by lower chloride and higher bicarbonate contents compared with the parent water. The decrease in chloride and increase in bicarbonate concentrations in these waters result from the dilution of the deep chloride-rich hydrothermal solution by a cold ground water before subsurface boiling (Truesdell and Thomp-

son, 1982; Kennedy et al., 1987). At Lower Geyser Basin the extent of dilution increases from the north (represented by Azure Spring and Ojo Caliente Spring) to south (represented by Octopus Spring), resulting in a concomitant decrease in the degree of subsurface boiling (Kennedy et al., 1987). At Upper Geyser Basin the waters discharged at Chinaman Spring, Ear Spring, Giantess Geyser, and Three Sisters Spring are the least diluted, while the waters are heavily diluted at Punch Bowl Spring and Sapphire Spring. The low concentrations in both bicarbonate and chloride in Sulphide Spring can be attributed to the dilution with cold ground water after subsurface boiling (Kennedy et al., 1987). Beneath these geyser basins, the shallow reservoirs have an estimated maximum temperature between 200 and 215°C. In contrast, the chloride waters dis-
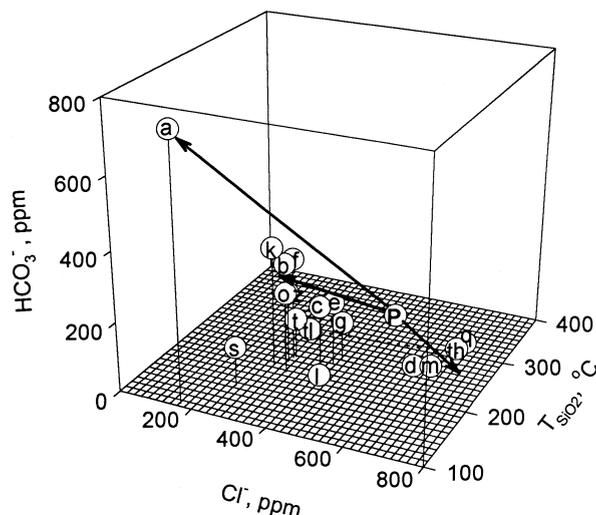
Fig. 2. Chloride, bicarbonate vs. subsurface temperature for selected chloride and sulfate-chloride springs sampled in this study in comparison with the "parent" water of the YNP hydrothermal system. Subsurface temperatures were estimated from silica geothermometry (Arnorsson, 1985). (a) Angel Terrace Spring, (b) Punch Bowl Spring,* (c) Chinaman Spring,* (d) Cinder Pool, (f) Sapphire Spring,* (g) Giantess Geyser,* (k) Octopus Spring,* (l) Perpetual Spouter,* (m) Emerald Spring,* (o) Ojo Caliente Spring, (p) Parent Water of Fournier, 1989, (q) Porkchop Spring,* (s) Sulphide Spring,* (t) Three Sisters Spring,* (th) Cistern Spring* with the highest Cl^-, (tl) Cistern Spring* with the lowest Cl^-, (z) Azure Spring. *Data from Thompson and Yadav (1979) and Thompson and DeMonge (1996).

charged at Norris Geyser Basin, represented by Porkchop Spring and Palpitator Spring, are enriched in chloride compared to the parent water but depleted in bicarbonate. This indicates that water discharging in Norris Geyser Basin has experienced extensive subsurface boiling and lost most volatile components (CO_2 and H_2S). No substantial dilution by cold water seems to take place before subsurface boiling, because once the bicarbonate is formed (from cold water dilution) it remains in solution (Kennedy et al., 1987) unless calcite precipitation occurs. The estimated maximum temperature for the shallow reservoirs which supply the neutral hot springs and geysers at Norris Geyser Basin ranges from about 200 to 325°C.

Hydrothermal water at Mammoth Hot Springs, as represented by Angel Terrace Spring in this study, is of the chloride-sulfate-bicarbonate type, different from those in the geyser basins. The temperature of Mammoth aquifer is less than 120°C. The chemical and isotopic data suggest, however, that the Mammoth hydrothermal water is also derived from the same parent water which feeds other geyser basins (Mariner et al., 1992). The distinct chemistry of Mammoth water has been attributed to the interaction of the hydrothermal solution with a thick sequence of sedimentary rock through which the hydrothermal solution flows to the surface combined with substantial dilution by cold ground water (Mariner et al., 1992).

Sulfate and dissolved sulfide are usually the most abundant aqueous sulfur species in hydrothermal solutions. The H_2S concentration of the YNP hydrothermal waters is typically less than 50 to 100 μmol/L (Thompson et al., 1975; Thompson and Yadav, 1979; Thompson and DeMonge, 1996). The sulfate concentrations span a wide range from a tenth of a mmol/L to

tens of mmol/L (see Table 1). The highest sulfate concentrations are found in acid-sulfate waters with low chloride content (e.g., Frying Pan Spring and Washburn Springs in Table 1). This type of water originates from the subsurface boiling of chloride-rich neutral water. Steam and H_2S separate from the underlying chloride water; the steam in part condenses, and H_2S is oxidized to sulfate either inorganically or microbiologically (White et al., 1971, 1988). The lowest sulfate concentrations are found in low-sulfate high-chloride waters discharged at Norris Geyser Basin, i.e., Porkchop Spring ($Cl^-/SO_4^{2-} = 72.5$). The average Cl^-/SO_4^{2-} ratios for waters in Upper and Lower Geyser Basins are about 36 and 25, respectively. Norris waters are characterized by a wide range of Cl^-/SO_4^{2-} ratios (see Table 1), which has been interpreted as the result of mixing of chloride water and acid-sulfate waters (Fournier, 1989). In addition, large temporal variations in the Cl^-/SO_4^{2-} ratio were observed for a single spring at Norris Geyser Basin (Fournier et al., 1992; Thompson and DeMonge, 1996). Fournier et al. (1992) pointed out that the quantity of sulfate discharged at Norris Geyser Basin is too large to be accounted for solely by present-day local oxidation of H_2S. It was suggested that microbial oxidation of native sulfur at the cooling margins of the basin could form an additional source of sulfate for the waters. The native sulfur may be old solfataras buried at relatively shallow depths in the basin (Mosser et al., 1973; Fournier et al., 1992, 1998). Fournier et al. (1992) suggested that the additional sulfate at Norris Geyser Basin may also be generated from the hydrolysis of magmatic SO_2 gas.

Sulfur isotopic compositions of sulfate, H_2S, and elemental sulfur in the YNP were studied by Truesdell et al. (1978) and more recently by Fournier et al. (1998). They found significantly different sulfur isotopic compositions for sulfate in springs with a low Cl^-/SO_4^{2-} ratio (<3) compared to that for sulfate in springs with a high Cl^-/SO_4^{2-} ratio (>54). Sulfate in springs with a high Cl^-/SO_4^{2-} ratio has $\delta^{34}S$ values around $+18$‰. This isotopic composition is thought to represent deep sulfate in isotopic equilibrium with H_2S ($\delta^{34}S = 0$%) at 360°C. Sulfate in springs with a low Cl^-/SO_4^{2-} ratio has $\delta^{34}S$ values around 0‰. The sulfate in these spring is attributed to nonequilibrium oxidation of H_2S at lower temperatures.

The aqueous sulfur species other than sulfate and dissolved sulfide, such as dissolved elemental sulfur, sulfite, thiosulfate, and polythionates are typically not included in conventional geochemical investigations of hot spring waters. These species, however, were studied by a few investigators at the YNP. Zinder and Brock (1977) measured sulfur dioxide and dissolved elemental sulfur in the YNP hydrothermal waters (mainly sulfide-rich acidic waters) and gases. No SO_2 was found in gases emanating from hot springs or fumaroles, but small amounts of SO_2 (typically less than 1.5 μmol/L) were detected in most of the sampled waters. The concentration of dissolved elemental sulfur can reach mmol/L levels in acid sulfate waters, but in alkaline waters the S(0) concentration is less than 3 μmol/L. Allen and Day (1935) detected thiosulfate in alkaline chloride springs of the YNP at concentrations from 20 μmol/L up to 175 μmol/L, much higher than H_2S concentrations. However, the analytic procedure adopted by Allen and Day (1935) tends to lead to an over-estimation of the thiosulfate concentration. The analysis was conducted a long time after sampling; hence, the oxidation of dissolved sulfide during the

Table 1. Thiosulfate, polythionate, dissolved sulfide, sulfate, chloride, and dissolved oxygen in selected geysers and hot springs of Yellowstone National Park

Spring	T °C	pH	D.O. μmol/L	$S_2O_3^{2-}$ μmol/L	#$S_2O_3^{2-}$ μmol/L	$S_nO_6^{2-}$ μmol/L	H_2S μmol/L	SO_4^{2-} mmol/L	Cl^- mmol/L	$\otimes Cl^-/SO_4^{2-}$
Punch Bowl Spring	93.0	7.0	n.a.	0.7	8.9	n.a.	1.5	0.265	8.141	30.7
Sapphire Spring	86.0	7.5	n.a.	1.0	17.9	n.a.	0.9	0.177	8.676	49.0
Giantess Geyser	91.5	7.2	n.a.	0.8	26.8	n.a.	33.5	0.263	12.00	45.6
Ear Spring	93.0	7.5	n.a.	n.a.		n.a.	28.2	0.288	11.77	40.8
Sulphide Spring	89.0	7.8	n.a.	0.7		n.a.	36.8	0.335	6.761	20.1
Three Sisters Springs	65.5	8.2*	n.a.	0.9		n.a.	n.a.	0.207	8.817	42.6
Basin Spring	71.2	8.4*	n.a.	0.5		n.a.	n.a.	0.253	7.831	31.4
Trail Geyser	85.5	7.6*	n.a.	0.1		n.a.	n.a.	0.483	9.183	19.2
Chinaman Spring	93.0	7.0	<3	2.5		n.a.	n.a.	0.244	10.68	43.5
Bowtie Spring	93.0	7.8	<3	1.3		n.a.	n.a.	0.260	8.592	33.0
Ojo Caliente Spring	93.0	7.8	3.1	2.4	44.6	n.a.	32.1	0.216	9.127	42.2
Azure Spring	84.2	8.7	0.0+	55		n.a.	10.6	0.427	8.620	20.2
Diadem Spring	60.4	7.9*	n.a.	0.7		n.a.	0.9	0.225	8.901	38.9
Unnamed Spring 150 m S. of Azure	89.0	7.8*	n.a.	8.2		n.a.	41.8	0.469	8.394	17.9
Bath Spring	91.8	7.3*	n.a.	9.3		n.a.	62.6	0.349	8.535	24.6
Cavern Spring	74.7	n.a.	n.a.	1.3		n.a.	4.4	0.304	6.901	22.7
Azure Satellite Spring 1	89.6	8.5*	0.0+	8.5		n.a.	9.4	0.599	8.507	14.2
Azure Satellite Spring 2	56.8	8.6*	n.a.	10.2		n.a.	4.1	0.458	8.310	18.1
Unnamed Spring 40 m N. of Azure	87.2	n.a.	n.a.	15.8		n.a.	12.9	0.578	8.873	15.4
Octopus Spring	83.5	7.2+	0.0+	<0.1		n.a.	n.a.	0.206	7.775	36.2
Cinder Pool	92.0	4.22	15.6	37.5**		8.00**	47.1	1.000	16.93	16.9
Horseshoe Spring	91.3	2.77	n.a.	2.0		<0.5	n.a.	1.842	10.50	5.7
Constant Geyser	61.0	3.57	n.a.	0.00		<0.5	n.a.	1.026	15.43	15.0
Emerald Spring	89.0⊕	3.5⊕	n.a.	<0.1		<0.5	n.a.	1.152	18.09	16.0
Cistern Spring	91.0	6.10	n.a.	70.8		<0.5	n.a.	0.932	12.14	13.0
Unnamed Spring	67	5.9	n.a.	95.0		<0.5	5.0	0.57	11.52	20.21
Palpitator Spring	84.0	6.67	n.a.	1.0		<0.5	n.a.	0.284	18.39	64.7
Fearless Geyser	91.5	5.75	n.a.	7.8		<0.5	n.a.	0.829	16.82	20.3
Perpetual Spouter	87.3	4.80	n.a.	<0.1		<0.5	n.a.	1.258	11.47	9.11
Porkchop Spring	50.0	7.00	n.a.	<0.1		<0.5	n.a.	0.274	19.89	72.5
Big Alcove Spring	93.5	5.80	n.a.	5.5		<0.5	n.a.	0.795	9.070	11.4
Echinus Geyser	85.0	3.53	n.a.	0.4		<0.5	0.9	3.083	3.070	1.00
Black Pool Spring	89.2	2.61	n.a.	0.2		<0.5	4.7	3.125	13.04	4.16
Unnamed, Norris Basin	93.0	1.65	n.a.	1.4		<0.5	n.a.	12.60	0.169	0.013
Frying Pan Spring	78.2	2.34	75	5.63		<0.5	30.3	4.552	0.254	0.055
Angel Terrace Spring	72.2	6.43	15.6	<0.1		<0.5	88.5	5.698	4.648	1.225
Acid Inkpot Washburn Springs	75.5	2.92	n.a.	0.9		<0.5	235.3	33.43	0.282	0.012
Rainbow Spouter Washburn Springs	93.0	6.71	n.a.	1.2		<0.0	<0.9	13.33	0.056	0.004
Unnamed Sp., Washburn Springs	82.0	1.83	n.a.	1.8		<0.0	167.7	43.75	0.197	0.005
Unnamed Sp., Washburn Springs	67.5	2.00	n.a.	0.9		<0.5	73.5	25.63	0.253	0.010

#: Data from Allen and Day (1935); +: data from Stauffer et al. (1980); ⊕ data from Thompson et al., (1975); *: pH measured in laboratory; $: reported as tetrathionate; ⊗ molar ratio; **: highest concentration; n.a.: not analyzed.

sample storage was virtually inevitable (the report by Allen and Day (1935) does not state explicitly whether thiosulfate analysis was done on site or in the laboratory, but the nature of the writing would suggest that it was done in the field laboratory, at least a day or more after sampling). The over-estimation of thiosulfate in the study by Allen and Day (1935) is consistent with the underestimation of dissolved sulfide compared with later studies (e.g., Thompson et al., 1975; Thompson and Yadav, 1979), since the H_2S concentrations in the study by Allen and Day (1935) were derived from the difference between thiosulfate and the sum of sulfide and thiosulfate determined by iodine titration.

No thiosulfate data of the YNP hydrothermal waters has been reported after the study by Allen and Day (1935). In this study, thiosulfate concentrations were determined for all major types of YNP hydrothermal waters. To avoid the problems upon storage of samples as encountered by Allen and Day (1935), the analyses in this study were conducted on site in a

mobile laboratory. Furthermore, this study was not restricted to alkaline waters as in the work by Allen and Day (1935); acid sulfate and acid sulfate-chloride waters were also sampled. In addition, polythionate was analyzed for waters at Norris Geyser Basin and Washburn Springs. To our knowledge this is first time the YNP waters have been analyzed for polythionates.

3. SAMPLING AND ANALYSES

Sampling of waters containing thiosulfate and polythionates as well as analyses for these metastable sulfoxyanions is nontrivial. The oxidation of H_2S, a common sulfur component in hydrothermal solutions, readily generates thiosulfate and probably other intermediate sulfur compounds. It is an accepted procedure to add a Cd^{2+} or Zn^{2+} solution upon sampling to precipitate sulfide (Moses et al., 1984; Vivit et al., 1984; Schoonen, 1989). The CdS and ZnS precipitates, however, are unstable photochemically in aqueous solutions. Illuminated with light of the appropriate wavelength, ZnS ($\lambda < 320$ nm) and CdS ($\lambda < 520$ nm) can be photo-oxidized by weak oxidants such as CO_2 and H_2O (Reber and Meier, 1984; Kanemoto et al., 1992) to aqueous sulfoxya-

nions. Furthermore, dissolved oxygen may slowly oxidize the metal-sulfide precipitates yielding sulfoxyanions (Goldhaber, 1983). Pyrite and sphalerite can also catalyze the oxidation of aqueous thiosulfate to tetrathionate by dissolved oxygen, even in the dark (Xu and Schoonen, 1995; Xu et al., 1996). Hence, complete stabilization of intermediate sulfur species through sulfide precipitation is problematic. Although this method may not cause large errors for the analysis of major species, such as sulfate, it certainly becomes a serious problem for the analysis of intermediate sulfur species, which are typically present at trace levels. Unfortunately, no other convenient sulfide stabilization method is yet available for water sampling. One can only curtail the photo-oxidation of the precipitates and/or the metal-sulfide catalyzed oxidation of aqueous sulfur species by choosing metal sulfides which have the lowest catalytic activity and the highest photochemical stability. More importantly, conducting the analyses on site, immediately after the collection of the sample, avoids storage of the sample which leads to changes in the sulfoxyanion speciation.

Cunningham et al. (1996) and Schoonen et al. (written commun.,1997) describe the effect of storage and sample preservation in more detail. In this study, a $ZnCl_2$ solution was used as the H_2S removal agent. ZnS photo-oxidation can only be induced by UV light because of its large bandgap energy (3.9 eV) (by contrast CdS can be photo-oxidized by irradiation with visible light because of a smaller bandgap, 2.4 eV). In addition, because of the high energy of its conduction bandedge, ZnS does not catalyze the reaction between thiosulfate and dissolved oxygen (Xu et al., 1996). Hence, ZnS is a better H_2S removal agent than CdS, despite the greater solubility of ZnS. To limit photochemical decomposition even further, water samples were stored in amber glass bottles. The storage time was kept as short as practically possible by analyzing the samples on site.

Various sampling techniques were used to retrieve water from springs. For small and nonviolent 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 µm) 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 were immediately withdrawn from the thermos can using the same method as for the nonviolent features.

To determine thiosulfate concentration, samples were collected in a 30 mL amber glass bottle containing 1mL of a 1 M $ZnCl_2$ 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 µm 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 min. Using a conductivity detector, the detection limit for thiosulfate is 0.1 µmol/L . The analyses were conducted on site in a mobile laboratory. Except for samples collected at Washburn Springs, the analysis was usually performed within 2 to 30 min after sampling. Samples collected at Washburn, a remote area in the northeastern section of the YNP, were assayed 2 to 3 h after sampling.

Samples for polythionate analysis were collected in 30 mL amber glass bottles containing 1 mL of 1M $ZnCl_2$, 1 mL of 1 M NaOH, and 1 mL 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 cyanolysis of polythionate generates thiocyanate and thiosulfate according to

$$S_nO_6^{2-} + (n-3)CN^- + H_2O = S_2O_3^{2-}$$
$$+ SO_4^{2-} + (n-3)SCN^- + 2H^+ \quad (1)$$
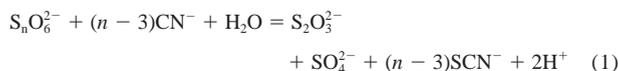
The polythionate concentration is then determined from the difference in thiosulfate concentration between the cyanolyzed and uncyanolyzed samples; the average chain length is determined from the resulting thiocyanate and thiosulfate concentration. The same IC configuration for thiosulfate was used for polythionate analyses. The detection limit of thiocyanate was 0.5 µmol/L, and the retention time is about 6 min. Since polysulfide, subjected to cyanolysis, will generate thiocyanate, those waters analyzed for polythionates were checked for the presence

of polysulfide. No polysulfides were found by on-site direct spectrophotometry.

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 21–0.03 µmol/L, and some samples had to be diluted. Dissolved oxygen was measured using the Winkler method; the fixed samples were titrated typically within 2 h of collection.

4. RESULTS

The $S_2O_3^{2-}$, $S_nO_6^{2-}$, H_2S, and SO_4^{2-} concentrations for thirty-nine hot springs of the YNP are given in Table 1. For clarity, the results will be examined in detail as three groups: (1) Upper and Lower Geyser Basin and Mammoth Hot Spring Area, (2) Norris Geyser Basin, and (3) Washburn Mountain Area and Frying Pan Hot Spring.

4.1. Upper and Lower Geyser Basin and Mammoth Hot Springs Area

In fourteen of twenty alkaline chloride springs in Upper and Lower Geyser Basin investigated in this study, thiosulfate was detected at concentrations less than 2.5 µmol/L, much lower than the concentrations of dissolved sulfide in these springs, and in six springs $\geq$ 9 µmol/L, higher than the concentration of H_2S in these springs.

Ojo Caliente, representative of 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 http://sbmp97.ess.sunysb.edu/). The water in the pool contains 32.1 µmol/L sulfide, but only 2.4 µmol/L thiosulfate and 3.1 µmol/L dissolved oxygen. As the water discharges into the drainage, the dissolved oxygen content increases rapidly (Fig. 3a). As a result, sulfide is oxidized to thiosulfate and sulfate. Sulfide decreases at an average rate of about 1.56 µmol/L s^{-1}, while thiosulfate forms at an average rate of 0.09 µmol/L s^{-1}. Sulfate increases at a rate about 0.21 µmol/L 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.

Another good example of the rapid formation of thiosulfate via dissolved sulfide oxidation by atmospheric oxygen is illustrated by the results of our study of Angel Terrace Spring at Mammoth Hot Springs. In the orifice of this spring, the thiosulfate is below the detection limit (<0.1 µmol/L), yet within 1 m of the orifice ($\leq$1 s travel time down a waterfall), the thiosulfate concentration increased to 4.5 µmol/L along with a rapid increase of dissolved oxygen concentration (see Fig. 3b).

Six out of eight springs sampled in the vicinity of Azure Spring in River Group of Lower Geyser Basin contain thiosulfate at concentrations between 7.1 and 55 µmol/L, values which are higher than the dissolved sulfide concentrations of these springs. Azure Spring is an intermittent hot spring which discharges alkaline bicarbonate-chloride water at a maximum flow rate of 2 L s^{-1} . Temperature fluctuations between 60 to 87°C have been observed. The duration of an active cycle is about two to three h. The sulfur speciation of Azure Spring water shows variability; however, the relationship between discharge conditions and sulfur speciation is not simple. Shown
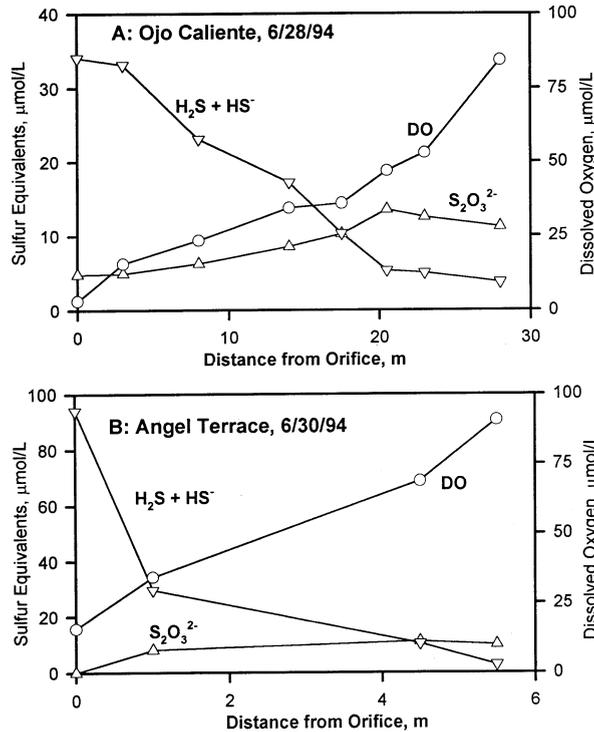
Fig. 3. Thiosulfate, sulfide, and dissolved oxygen concentrations along the drainage of Ojo Caliente (A) and Angel Terrace Spring (B). Concentrations expressed in sulfur equivalents, molar concentration multiplied by the number of sulfur atoms in S-containing species.

in Fig. 4 are the changes in concentrations of thiosulfate and dissolved sulfide as a function of time for three active cycles. On August 19, 1995, Azure Spring water sampled at the overflow had both high thiosulfate (55 μmol/L) and high dissolved sulfide (37.5 μmol/L) during the surging period of the spring, but decreased thiosulfate (15 μmol/L) and decreased dissolved sulfide (6.3 μmol/L) during low-flow phase. On Aug. 20, 1995, overflow water contains both thiosulfate and dissolved sulfide that varied only slightly during the active cycle. But the highest thiosulfate and dissolved sulfide concentrations coincides with the maximum in discharge and temperature. On Aug. 18, 1996, the water was sampled with a thermos can at a depth of about 1.5 m in the pool. Both surging phase and no-flow phase have temporally consistent thiosulfate concentrations ($\sim$50 μmol/L). The dissolved sulfide concentrations measured during the surging phase ($\sim$11 μmol/L) are, however, much higher than those measured during the quiet phases ($\leq$3μmol/L).

Changes in thiosulfate and dissolved sulfide concentrations along the drainage of Azure Spring are shown in Fig. 5. 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 and $S_2O_3^{2-}$ much higher at Azure than at Ojo Caliente or Angel Terrace. Sulfide concentrations for Azure Spring may depend upon the balance between input flow rate and volatilization rate. When the pool surges, input rate is greater than volatilization rate and H_2S concentrations increase. This process
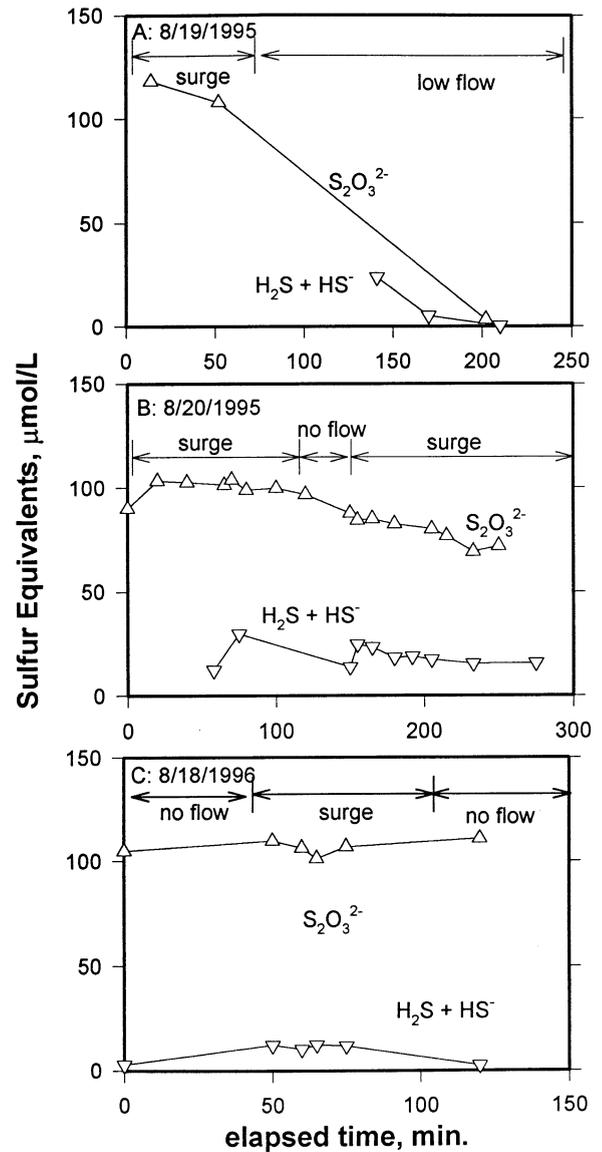

Fig. 4. Thiosulfate, dissolved sulfide concentration as a function of time for Azure Spring for three sampling periods. Samples shown in panels A and B were taken at the overflow of the spring; samples in panel C were taken from the middle of the pool.

would not necessarily affect thiosulfate concentrations. During low-flow or no-flow conditions, H_2S volatilization would dominate and H_2S concentrations would decrease.

4.2. Norris Geyser Basin

Fourteen springs were sampled in Norris Geyser Basin. The highest thiosulfate concentrations (71 and 95 μmol/L) of all springs sampled in this study was obtained in Cistern Spring and an unnamed spring located between Cistern Spring and Echinus Spring. Both springs are sulfate-chloride springs with the pH of about 6.0. Two sulfate-chloride springs with pH $>$ 5.0 (Big Alcove Spring and Fearless Geyser) have thiosulfate concentration in the range of 5.4 to 8 μol/L, whereas

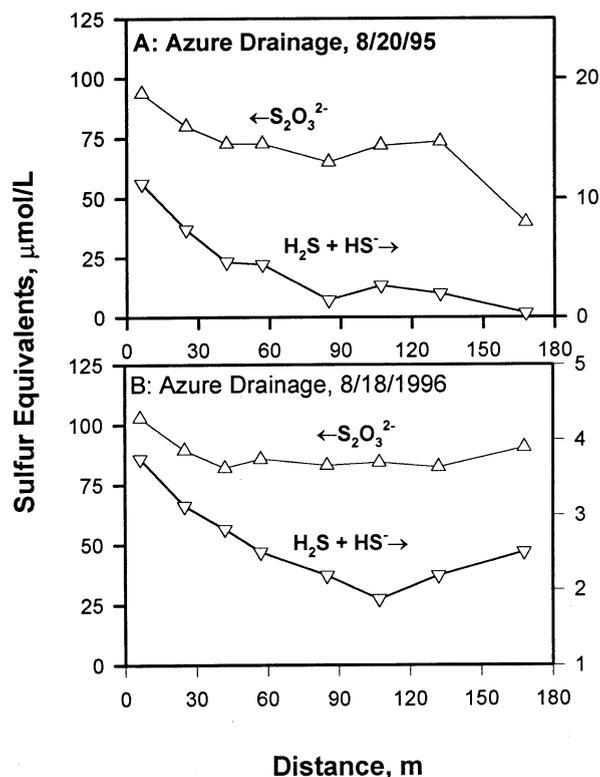Fig. 5. Thiosulfate and dissolved sulfide concentrations as a function of distance along the drainage of Azure Spring.

Fig. 6. Thiosulfate and dissolved sulfide concentration and temperature as a function of distance along the drainage of Frying Pan Hot Spring.

five of six sulfate-chloride springs with pH < 5.0 (Echinus Geyser, Horseshoe Spring, Constant Geyser, Emerald Spring, and Perpetual Spouter) have thiosulfate concentrations near the detection limit (0.1 μmol/L). The only sulfate-chloride spring with pH < 5 which contains a significant amount of thiosulfate is Cinder Pool. No thiosulfate was detected in the acid-sulfate springs (Black Pool and Boiling Amber Spring). And as in Upper and Lower Geyser Basin, no significant amount of thiosulfate was identified in near-neutral chloride springs with low sulfate (Porkchop Spring and Palpitator Spring).

All waters sampled in Norris Geyser Basin were analyzed for polythionate. Polythionate was found only in Cinder Pool. The concentrations varied from below detection (0.5 μmol/L) to 8 μmol/L. The average length of the sulfur chain of the polythionate was 4.1 to 4.9. Cinder Pool has not only a unique speciation of aqueous sulfoxyanions, but also peculiar sulfur features, namely the floating sulfur spherules and a subsurface molten sulfur layer (White et al., 1988). Additional laboratory experiments were conducted to investigated the effects of the presence of the molten sulfur pool and sulfur spherules on the aqueous sulfur speciation in Cinder Pool. 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 via the oxidation of thiosulfate by dissolved oxygen, a reaction catalyzed by the sulfur spherules covering part of the pool. The results of these experiments and a detailed description of sulfur speciation in
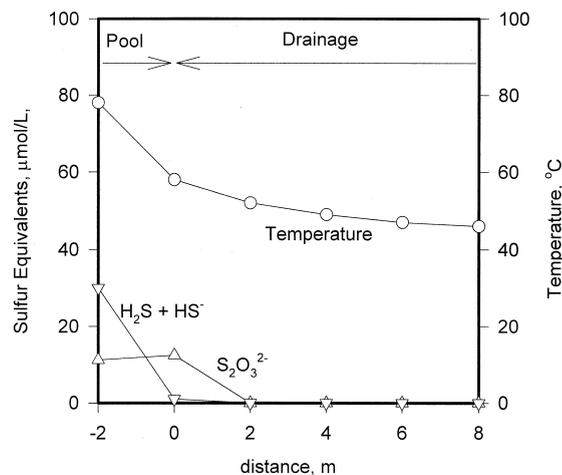
Cinder Pool will be reported in a separate contribution (Xu, 1997).

4.3. Washburn Springs and Frying Pan Hot Spring

In addition to the two acid sulfate springs in Norris Basin, five acid-sulfate springs in the Washburn Mountain Area and Frying Pan Area were sampled in this study. Frying Pan Spring contained 6.25 μmol/L thiosulfate, whereas in the Washburn Springs the thiosulfate concentration was around 0.9 μmol/L. Figure 6 shows the changes in thiosulfate and H_2S concentrations along the drainage of Frying Pan. In contrast to the neutral-alkaline chloride springs, thiosulfate decomposes rapidly after the water discharges from the pool into the drainage.

5. DISCUSSION

The thiosulfate concentrations of Yellowstone alkaline chloride waters obtained in this study are much lower than those reported by Allen and Day (1935). For example, Allen and Day (1935) reported thiosulfate concentrations of 9 to 45 μmol/L for Ojo Caliente Spring, Sapphire Spring, Giantess Geyser, and Punch Bowl Spring; while we detected only 0.7 to 2.4 μmol/L in these springs (see Table 1). By contrast, concentrations for major constituents, such as chloride, in these springs obtained in this study are in excellent agreement with those reported by Allen and Day (1935). Because Allen and Day (1935) did not examine acid springs, the comparison between our results and theirs is restricted to neutral and alkaline springs. Allen and Day (1935) assumed that thiosulfate is not stable in acid springs and, therefore, they only analyzed neutral to alkaline springs for this sulfoxyanion. The results of this study show, however, that the thiosulfate concentrations in acid springs are comparable to those in many alkaline springs.

In the following sections, the correlation of thiosulfate with dissolved sulfide and sulfate as well as the origin of thiosulfate in hydrothermal waters will be discussed. For the discussion of the origin of the thiosulfate, three different processes will be

evaluated: H_2S oxidation, SO_2 hydrolysis, and elemental sulfur hydrolysis.

5.1. Correlation Between Thiosulfate and Dissolved Sulfide

On the basis of the observation that thiosulfate is a common oxidation product of dissolved sulfide, a negative correlation of these two species would be expected. Such a correlation exists when H_2S concentrations are greater than $S_2O_3^{2-}$ concentrations, the more common condition found at the YNP. This condition would lead to $S_2O_3^{2-}$ concentrations increasing as H_2S concentrations decrease through volatilization and oxidation during downstream transport. Ojo Caliente and Angel Terrace drainages show this effect very well (see Figs. 3a and b). The less common condition, with initial $S_2O_3^{2-} > H_2S$, would mean that any thiosulfate formed from sulfide oxidation might not be detected during downstream transport and their relative proportions would depend on discharge rates of the hot spring and H_2S volatilization rate (a function of pH, temperature, wind speed, and turbulence). Hence, no correlation between H_2S and $S_2O_3^{2-}$ concentrations would be apparent. Azure Spring drainage shows this effect very well. What remains puzzling is that Ojo Caliente and Azure Spring have significantly different sulfur speciations, while other major constituents are nearly identical in concentration. Particularly striking are the much higher sulfate content and total sulfur content (i.e., sum of sulfur species) in Azure Spring. The factors that lead to a given total sulfur content and the speciation of this sulfur in a hot spring discharge at its source is a complex function of hydrogeochemical conditions in the subsurface and will be discussed in sections, 5.2 and 5.3.

5.2. Correlation Between Thiosulfate and Sulfate

There appears to be a relationship between thiosulfate concentrations and sulfate concentrations. This is illustrated in Fig. 7 where thiosulfate concentrations are plotted vs. the Cl^-/SO_4^{2-} ratio. Thiosulfate concentrations are below or near the detection limit (0.1 μm L^{-1}) in chloride waters with high Cl^-/SO_4^{2-} ratios (i.e., waters with relatively low SO_4^{2-} concentrations). The high-thiosulfate springs, on the other hand, tend to be sulfate-enriched chloride springs. The mean Cl^-/SO_4^{2-} ratio of the six high-thiosulfate springs in the River Group of Lower Geyser Basin is 18.2, significantly lower than the mean Cl^-/SO_4^{2-} ratios of the waters of other springs in Lower Geyser basin (average $Cl^-/SO_4^{2-} = 30$ for thirty-six springs excluding springs in the River Group, Thompson and Yadav, 1979) and Upper Geyser Basins (average $Cl^-/SO_4^{2-} = 35$ for 10 springs, this study) (see Table 1). In Norris Geyser Basin, thiosulfate also tends to be high in sulfate-chloride waters, but depleted in springs with low sulfate concentrations. This suggests that the process or processes that generate high thiosulfate concentrations also generate sulfate. However, high sulfate concentrations are not always accompanied by high thiosulfate concentration. For example, Angel Terrace of Mammoth Spring is a neutral chloride water enriched in both sulfate and dissolved sulfide, but it contains no measurable thiosulfate at the orifice. Low pH sulfate-chloride waters at Norris Geyser basin and acid sulfate waters are also depleted in thiosulfate. These acid sul-
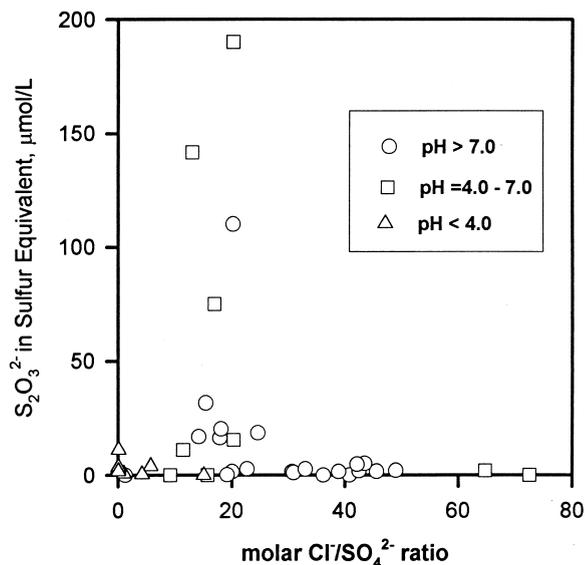

Fig. 7. Thiosulfate concentration vs. molar chloride/sulfate ratio for selected YNP springs.

fate waters form as fluids rich in H_2S reach the shallow subsurface or the surface and rapidly oxidize to elemental sulfur. The sulfur oxidizes more slowly to sulfuric acid and increases the sulfate content of the hot springs. The oxidation of H_2S generates acidity which lowers the pH of the water, unless the acidity is neutralized by water-rock interaction with carbonate minerals. Angel Terrace at Mammoth Hot Springs is a water in which the acidity generated by sulfide oxidation does not lead to a low pH due to the presence of carbonate rocks (Fournier, 1989).

5.3. The Origin of Thiosulfate

The enrichment of thiosulfate in slightly acidic to alkaline chloride waters which are also enriched in sulfate suggests that thiosulfate formation is associated with 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, 1997), and (3) hydrolysis of elemental sulfur at elevated temperature (Robinson, 1973; Giggenbach 1974a, b; Rafal'sky et al., 1983; Dadze and Sorokin, 1993; Xu, 1997). Each of these processes will be briefly discussed. Furthermore, we will evaluate the importance of each of these three thiosulfate-forming processes in the YNP hydrothermal system.

5.3.1. H_2S oxidation as a source of thiosulfate

The oxidation of dissolved sulfide in hydrothermal solutions may take place via three pathways: (1) exposure of hydrothermal water to atmospheric oxygen upon discharge, (2) subsurface mixing of sulfide-containing hydrothermal solutions with aerated ground water, and (3) oxidation after the collection of samples as a result of entrainment of atmospheric oxygen

during sampling. In this study, thiosulfate formation via the third pathway was minimized by the rapid, on site analyses. Hence, the third pathway is not further considered. The discussion of the first pathway is restricted to thiosulfate formation in the main pool, the formation of thiosulfate via this mechanism in the drainages has already been addressed.

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 surface or near-surface oxidation of dissolved sulfide in hot springs is not an effective mechanism for thiosulfate formation. This observation appears to contradict the experimental data that H_2S oxidation leads to thiosulfate formation (O'Brien and Birkner, 1977; Zhang and Millero, 1993). However, the conditions in the hot springs are significantly different from those in experimental studies. The rate of thiosulfate formation via the reaction between dissolved sulfide and dissolved molecular oxygen shows a first-order dependence on the concentrations of both reactants. The oxygen concentrations and H_2S concentrations in the pools and orifices of the springs are far lower than those in most laboratory experiments. Furthermore, the continuous discharge of most hot springs limits the reaction time, which keeps the extent of the reaction to a minimum. Stauffer et al. (1980) reported that the rate of diffusion of molecular oxygen into the hot pools is the rate-controlling step in the oxidation of dissolved sulfide. The fact that in most springs sulfide is detectable but the dissolved oxygen levels are near-zero is consistent with this notion. As shown by our study of the changes in sulfur speciation in the drainages of Ojo Caliente Spring and Angel Terrace Spring, thiosulfate does form rapidly via sulfide oxidation as the waters pass through the drainages. The turbulent flow in these shallow drainages (not more than a few centimeters deep) and the cooling of the water enhance the rate of gas transfer between water and the atmosphere. Hence, the rate of ingassing of oxygen as well as the rate of outgassing of H_2S increases dramatically as the water enters the drainages. So, while thiosulfate formation via oxidation of sulfide is of importance in the drainages, it plays little or no significant role in the more quiet parts of the springs, including pools where the water first emerges from depth. Near surface oxidation processes can certainly not explain the high-thiosulfate springs found in Lower Geyser Basin and in Norris Geyser Basin.

The significance of deeper subsurface oxidation of dissolved sulfide (pathway 2) as a source of thiosulfate is difficult to evaluate. The waters discharged in Upper and Lower Geyser Basins are thought to be derived from a mixture of a deep hydrothermal solution (containing most of the volatile components, including H_2S) and a cold, oxygen-saturated ground water (Truesdell et al., 1978; Fournier, 1989). It is conceivable that thiosulfate forms in the subsurface by oxidation of sulfide as a result of this mixing. Certainly the occurrence of elemental sulfur in the shallow subsurface of the pool indicates that some H_2S oxidizes to elemental sulfur.
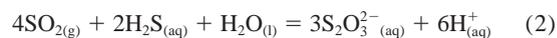
Some simple mass balances are useful in evaluating thiosulfate formation in springs in Upper and Lower Geyser Basin via subsurface oxidation of sulfide. The cold ground waters recharging the geyser basins infiltrate at about 2500 m altitude with an average temperature of 5°C and 0.28 mmol L^{-1} (9 mg L^{-1}) dissolved oxygen in solution (Truesdell et al., 1978). Taking this oxygen concentration, each liter of groundwater is

capable of producing a maximum of 0.14 mmol L^{-1} thiosulfate (i.e., assuming thiosulfate is the only product of sulfide oxidation and an unlimited supply of H_2S). While mixing of cold O_2-saturated water and a H_2S-rich hydrothermal water can account for the thiosulfate observed in Azure Spring, it cannot account for the enrichment in sulfate of about 0.2 mmol L^{-1} over Ojo Caliente (a nearby spring with essentially the same chloride and bicarbonate concentrations as Azure Spring). A liter of cold O_2-saturated water can only generate a maximum of 0.14 mmol L^{-1} sulfate via oxidation of H_2S. Ingassing of atmospheric oxygen in the shallow parts of the system could perhaps provide sufficient additional oxygen to generate the excess sulfate observed in Azure Spring. Assuming an adequate supply of oxygen, oxidation of 0.3 mmol L^{-1} H_2S would be sufficient to account for the observed thiosulfate concentration and sulfate enrichment in Azure Spring. The required amount of H_2S to produce the sulfoxyanion concentrations in Azure Springs is, however, much higher than the dissolved sulfide concentration in Ojo Caliente. Except for sulfate, the concentrations of major constituents are nearly identical in these two springs. Hence, it is not unreasonable to assume that these two waters are derived from the same parent water. If so, then the H_2S required to produce the sulfoxyanion concentrations in Azure Spring must be added to Azure Spring via a non-aqueous source. Ingassing of magmatic H_2S may provide hydrogen sulfide, but the condensation of associated water vapor would dilute the spring water (Fournier et al., 1998). Because there is no evidence for dilution in Azure Spring as compared to Ojo Caliente, it is unlikely that ingassing of magmatic H_2S is important in forming thiosulfate in Azure Spring. Hence, an alternative non-aqueous source must account for the observed thiosulfate and sulfate concentrations in Azure Spring.
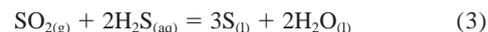
It is more difficult to explain the formation of thiosulfate at Norris Geyser Basin because volatiles were depleted from the hydrothermal solution by subsurface boiling, and little cold ground water enters the aquifer. The variability of thiosulfate concentration among these springs suggests that subsurface oxidation of sulfide by dissolved oxygen is not a dominant process, although contribution of minor thiosulfate cannot be excluded.

5.3.2. SO_2 hydrolysis as a source of thiosulfate

It is interesting to note that one of the mechanisms proposed by Fournier et al. (1992) to explain the origin of acid-sulfate-chloride water at Norris Geyser Basin—hydrolysis of magmatic SO_2 gas in hydrothermal solution—is also a process that may generate thiosulfate in large quantities. It is well known that magmatic SO_2 gas reacts with water rapidly at elevated temperature to form H_2SO_4 and H_2S (Holland, 1965; Rye et al., 1992; Giggenbach, 1987, 1997). When the magmatic gas dissolves in a H_2S-containing hydrothermal solution, however, the reaction between SO_2 and H_2S generates thiosulfate (Xu, 1997) and elemental sulfur:

$$4SO_{2(g)} + 2H_2S_{(aq)} + H_2O_{(l)} = 3S_2O_3^{2-}{}_{(aq)} + 6H^+_{(aq)} \quad (2)$$

and

$$SO_{2(g)} + 2H_2S_{(aq)} = 3S_{(l)} + 2H_2O_{(l)} \quad (3)$$

There is, however, little direct evidence to support a significant

discharge of magmatic SO_2 gas into the hydrothermal system at the YNP. Furthermore, the composition of the gases evolved form the magma is expected to be rich in H_2S and poor in SO_2. Zinder and Brock (1977) investigated the occurrence of SO_2 in geothermal waters and gases discharged at Norris Basin, but did not find any indication of magmatic SO_2. Only small amounts of sulfite were detected in hot waters. The sulfite in these waters was considered to be the product of surficial H_2S oxidation. As pointed out in detail by Rye and Truesdell (1992, 1993), and Giggenbach (1997) magmas tend to evolve a gas mixture that is rich in H_2S ($f_{H_2S}/f_{SO_2} > 1$). Interactions with minerals subsequent to separation from the magma will tend to remove most if not all SO_2 before it can dissolve in the deepest zone of the hydrothermal system. This notion is consistent with the low sulfate concentration in the "parent" water at the YNP (Truesdell et al., 1978; Fournier et al, 1998). So based on the lack of evidence for direct SO_2 degassing and theoretical considerations, it is unlikely that the thiosulfate and excess sulfate present in many waters in Norris Geyser Basin originates from magmatic SO_2 degassing.

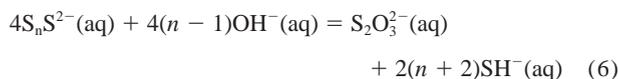*5.3.3. Sulfur hydrolysis as a source of thiosulfate*

One process which could result in local enrichment of thiosulfate as well as sulfate 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_8 opens and via a complex set of disproportionation reactions sulfide and sulfoxyanions form. Relatively little experimental work has been carried out to determine the kinetics and mechanisms of the disproportionation reaction. What is clear, however, is that the composition of the oxyanions formed during the disproportionation of elemental sulfur depends on the temperature and pH of the solution. Below 250°C and alkaline pH, the reaction between elemental sulfur and hydroxide leads to thiosulfate (Pryor, 1962; Giggenbach, 1974a). This reaction can be represented by

$$4S(l) + 3H_2O(l) = S_2O_3^{2-}(aq) + 2HS^-(aq) + 4H^+(aq) \tag{4}$$
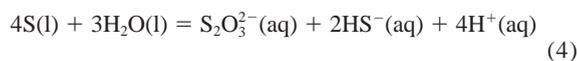
In acid solutions, sulfur hydrolysis proceeds to form sulfate (Oana and Ishikawa, 1966; Ellis and Giggenbach, 1971; Robinson, 1973):

$$4S(l) + 4H_2O(l) = 3H_2S(aq) + H_2SO_4(aq) \tag{5}$$

Giggenbach (1974a,b) showed that the disproportionation of polysulfide (S_n^{2-}), which itself is generated from the interaction between sulfide and elemental sulfur, yields thiosulfate and H_2S at temperatures between 100 and 240°C and pH above 6. The conversion between thiosulfate and polysulfides is reversible and can be represented by

$$4S_nS^{2-}(aq) + 4(n-1)OH^-(aq) = S_2O_3^{2-}(aq)$$
$$+ 2(n+2)SH^-(aq) \tag{6}$$

Furthermore, Dadze and Sorokin (1993) showed that thiosulfate is one of the major oxyanions formed in sulfur hydrolysis at temperatures up to 420°C. Recently, Xu (1997) demonstrated that thiosulfate is the predominant intermediate sulfoxyanion

formed from sulfur hydrolysis between pH 4 and 8, and temperature between 100 and 200°C.

While thiosulfate may readily form via sulfur hydrolysis, its persistence in a hydrothermal solution depends strongly on the pH of the solution (Pryor, 1960; Giggenbach, 1974a, b; Xu 1997). Thiosulfate is stable in alkaline solutions, but disproportionates in acid solutions (see e.g., Xu and Schoonen, 1995, and references therein). Hence, under the conditions prevailing in the shallow reservoir which supplies Azure Spring (~200°C, pH 8.0), thiosulfate could be formed if the hydrothermal solution comes into contact with elemental sulfur. Furthermore, buffering of the hydrothermal solution around pH neutral stabilizes thiosulfate formed via sulfur hydrolysis. When acidity generated from the sulfur hydrolysis exceeds the buffer capacity of the hydrothermal solution and pH falls to below pH neutral, then thiosulfate is expected to disproportionate according to (Johnson and McAmish, 1973):

$$S_2O_3^{2-} = SO_3^{2-} + S \tag{7}$$

$$3SO_3^{2-} + H_2O = 2SO_4^{2-} + S + 2OH^- \tag{8}$$
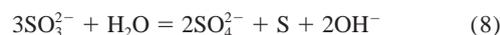
Hence, the limited stability of thiosulfate restricts the presence of this species to the very initial stage of sulfur hydrolysis (i.e., very low sulfur/solution ratio) in hydrothermal systems, with pH around neutral. As the residence time of the solution increases, more of the S-derived thiosulfate will be converted to sulfate (reaction 7 and 8). Consequently, sulfur hydrolysis is a process that leads to the addition of sulfur to a solution, with a sulfoxyanion speciation that may vary in hydrologic dynamic systems. The high sulfate and thiosulfate concentrations in Azure Spring may (in part) be due to sulfur hydrolysis. However, a higher dissolved sulfide concentration is expected for this water if sulfur hydrolysis is indeed important (reactions 4 and 6) unless the S-derived H_2S is (a) separated from the solution before it discharges or (b) oxidized before it discharges. It is also possible that some of the excess sulfate in Azure Spring may be originating from interaction of the water with sulfate-bearing minerals (this possibility occurred to us after reading the work by Fournier et al., 1998). The combination of interaction with sulfate-bearing minerals and elemental sulfur could explain the presence of thiosulfate and excess sulfate without high dissolved sulfide. Sulfate-bearing minerals such as alunite and jarosite are common in solfataras. Azure Spring is located near an explosion crater (Pocket Basin), which may contain some old solfatara deposits. 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. The fact that the highest thiosulfate occurs in a pH 6.1 sulfate-chloride spring, while thiosulfate is at or below the detection limit in sulfate-chloride springs with pH values below 5 (with the exception of Cinder Pool) can be explained by the limited stability of thiosulfate in acid waters. In addition, sulfur hydrolysis may also contribute to the origin of the acid-sulfate-chloride waters at Norris Geyser Basin. The acid-sulfate-chloride water underlies much of the Norris Geyser Basin and has temperatures between 200 and 220°C (Fournier et al., 1998). The origin of this type of water has been discussed in several studies (Truesdell et al., 1978; Fournier et al., 1992, 1998). Truesdell et al., (1978) suggested that this type of water orig-

inates from the oxidation of magmatic H_2S by an unlimited supply of dissolved oxygen at or near the surface, followed by downward percolation and mixing with the deeper chloride-rich neutral water. However, Fournier et al. (1992, 1998) questioned this notion. On the basis of the data by Truesdell et al. (1978) and new chemical and isotopic data, Fournier et al. (1992, 1998) have argued that the formation of the acid-chloride-sulfate water at Norris is probably due to the interaction of deep chloride-rich water with sulfate-bearing minerals and perhaps also elemental sulfur. As mentioned above solfatara deposits contain mostly elemental sulfur with some minerals such as alunite and jarosite. Fournier et al. (1998) pointed out that it is not unreasonable to expect buried solfatara deposits in the subsurface in the Norris area. Interaction with sulfate-bearing minerals may indeed be responsible for a considerable amount of the excess sulfate found in the waters at Norris, but sulfate-bearing minerals are not expected to yield thiosulfate upon water-rock interaction. Therefore, the presence of thiosulfate in some of the waters in Norris Geyser Basin indicates that that interaction with elemental sulfur does contribute to the formation of the acid-sulfate-chloride water at depth in Norris Geyser Basin.

One method to evaluate the extent of sulfur hydrolysis in the YNP system is to calculate the degree of saturation with respect to elemental sulfur in the hydrothermal waters. As suggested by Webster (1987), thiosulfate concentrations in hydrothermal systems may be controlled by sulfur hydrolysis (see Eqn. 4). On the basis of saturation calculations, Webster (1987) concluded that thiosulfate concentrations in the Taupo Volcanic Zone, New Zealand, are controlled by the equilibrium represented in Eqn. 4. The thiosulfate concentrations of most YNP waters are, however, far from saturation with respect to elemental sulfur. Shown in Fig. 8 is degree of saturation with respect to sulfur for hydrothermal waters of both the YNP and the Taupo Volcanic Zone, New Zealand (Webster, 1987) as functions of temperature and pH of each spring. The degree of saturation is defined as the ratio of ion activity products for those waters to the equilibrium constant of Eqn. 4. The equilibrium constants were calculated using SUPCRT92 described by Johnson et al. (1992). The results of these calculations show that acid sulfate waters with low thiosulfate concentrations (e.g., Frying Pan Spring, Washburn Springs) appear to be closest to equilibrium, while neutral and alkaline waters are far out of equilibrium with respect to reaction 4. A similar trend is seen in the data for hot springs in the Taupo Volcanic Zone. This trend arises from the fact that the sulfur solubility given by Eqn. 4 is highly pH dependent. For alkaline solutions, this equilibrium requires unrealistically high thiosulfate concentrations (e.g., several molar at pH 7); while for acidic solutions the saturation with respect to sulfur is reached at much lower thiosulfate concentrations (e.g., few μM at pH 2). Hence, it is unlikely that the sulfur hydrolysis/precipitation reaches equilibrium in deep hydrothermal solutions in either the YNP or the Taupo Volcano Zone where solutions are thought to be near neutral. The data obtained in this study, as well as those from Webster (1987) indicate that although sulfur hydrolysis is a plausible pathway for the generation of thiosulfate in hydrothermal solutions, it rarely reaches equilibrium.
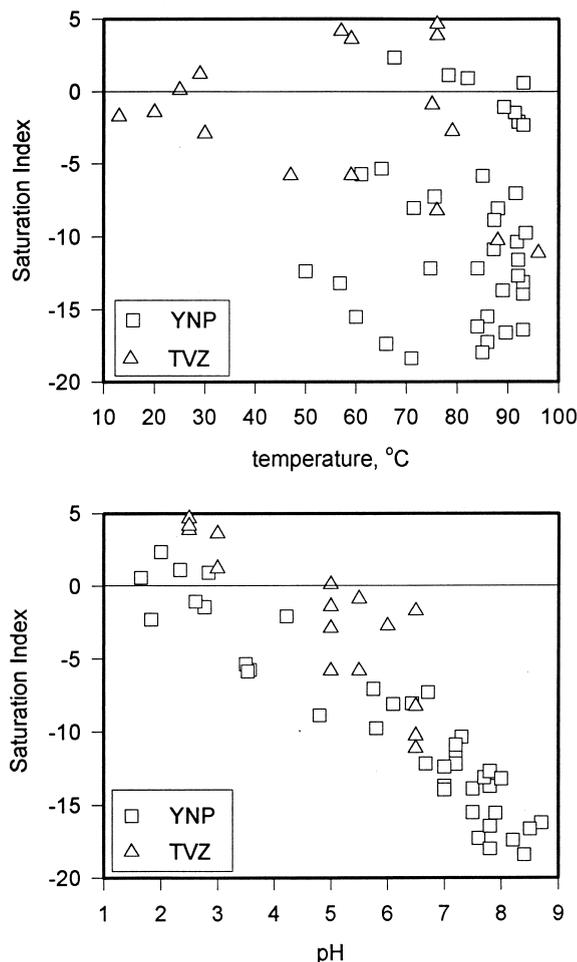

Fig. 8. Saturation index with respect to elemental sulfur as represented by Eqn. 4, for hot springs of the Yellowstone National Park (YNP) and the Taupo Volcanic Zone (TVZ) of New Zealand (Webster, 1987) as functions of temperatures (A) and pH (B) of springs. The Saturation Index is defined by $\log([S_2O_3^{2-}][HS^-]^2[H^+]^4/K)$, where K is the equilibrium constant of Eqn. 4 at the temperature of the spring, and $[S_2O_3^{2-}]$, $[HS^-]$ and $[H^+]$ are the concentrations of thiosulfate, bisulfide, and acidity, respectively. The bisulfide concentration was calculated from the measured concentration of total dissolved sulfide, pH, and temperature of the springs.

6. CONCLUSIONS

The analysis of thiosulfate, polythionate, dissolved sulfide, and sulfate in the YNP hydrothermal waters shows that the pH neutral and alkaline chloride waters with the lowest sulfate contents ($Cl^-/SO_4^{2-} > 27$), which are believed to represent the dominant water in the deep reservoirs of the hydrothermal system, have no appreciable amount of thiosulfate. Hence, thiosulfate is unlikely to be an abundant aqueous sulfur species in the deeper parts of the YNP hydrothermal system. Thiosulfate in excess of dissolved sulfide was detected in some sulfate-enriched chloride springs ($Cl^-/SO_4^{2-} = 13$ to 27) in Norris Geyser Basin and River Group of Lower Geyser Basin. Since the surface or near-surface oxidation of dissolved sulfide in the orifice or pool of a hot spring by atmospheric oxygen cannot produce significant amounts of thiosulfate, the thiosulfate in

these high-thiosulfate springs is believed to be of subsurface-origin. The sulfoxyanion speciation for the River Group in Lower Geyser Basin requires an additional source of S. One possibility is that the sulfoxyanion speciation in these waters results from the oxidation of sulfide. This requires, however, a combination of H_2S and O_2 ingassing. An alternative explanation is that the sulfoxyanion speciation in these waters results from sulfur hydrolysis combined with interaction with sulfate-bearing minerals. For one water in Norris Basin, Cinder Pool, there is conclusive evidence on the basis of earlier work that sulfur hydrolysis is important. In other high-thiosulfate springs within Norris Geyser Basin it is not clear whether the observed sulfoxyanion speciation results predominantly from sulfur hydrolysis or sulfide oxidation. SO_2 hydrolysis as a source of thiosulfate seems unlikely given earlier work on SO_2 concentrations in fumaroles, SO_3^{2-} concentrations in hot springs, and theoretical considerations of the H_2S/SO_2 gas ratio evolved from rhyolitic magmas.

Thiosulfate may, in general, form by surface, near-surface, or subsurface oxidation of H_2S as well as sulfur hydrolysis. However, it is clear that thiosulfate can only persist in neutral to alkaline solutions. The fact that most thiosulfate-minerals were identified in carbonate formations (Kucha, 1988; Kucha and Viaene, 1993), where an alkaline solution would be expected, is therefore not surprising.

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