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Thioarsenates in Geothermal Waters of Yellowstone National Park: Determination, Preservation, and Geochemical Importance

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Mono-, di-, tri-, and tetrathioarsenate, as well as methylated arsenic oxy- and thioanions, were determined besides arsenite and arsenate in geothermal waters of Yellowstone National Park using anion-exchange chromatography inductively coupled plasma mass spectrometry. Retention time match with synthetic standards, measured S:As ratios, and molecular electrospray mass spectra support the identification. Acidification was unsuitable for arsenic species preservation in sulfidic waters, with HCl addition causing loss of total dissolved arsenic, presumably by precipitation of arsenic-sulfides. Flash-freezing is preferred for the preservation of arsenic species for several weeks. After thawing, samples must be analyzed immediately. Thioarsenates occurred over a pH range of 2.1 to 9.3 in the geothermal waters. They clearly predominated under alkaline conditions (up to 83% of total arsenic), but monothioarsenate also was detected in acidic waters (up to 34%). Kinetic studies along a drainage channel showed the importance of thioarsenates for the fate of arsenic discharged from the sulfidic hot spring. The observed arsenic speciation changes suggest three separate reactions: the transformation of trithioarsenate to arsenite (major initial reaction), the stepwise ligand exchange from tri- via di- and monothioarsenate to arsenate (minor reaction), and the oxidation of arsenite to arsenate, which only becomes quantitatively important after thioarsenates have disappeared.

Introduction

Geothermal waters have long been known to contain elevated arsenic concentrations (*1*−*3*). After leaching from the host rocks, geothermal arsenic remains in the fluid phase during subsurface boiling. In 1888, geothermal water chemistry was studied across Yellowstone National Park (*4*), revealing arsenic concentrations as high as 5.4 mg/L in this residual fluid phase of near-neutral pH (*5*). Arsenic enrichment is observed following increased host-rock leaching in CO_2-rich waters (*6*) or leaching of precipitated arsenic-sulfides at or near the surface (*1*, *7*). Previous arsenic speciation studies on geothermal waters presumed arsenite predominance (H_3AsO_3) at the source, followed by rapid oxidation to arsenate (H_3AsO_4) in the discharge channels (*6*−*9*).

Recent studies (*10*−*15*) indicate that soluble arsenic-sulfur compounds may be important arsenic species in sulfide-rich waters which could have far-reaching hydrogeochemical implications, but such species have never been confirmed in geothermal waters. The identity of dissolved arsenic-sulfur species remains controversial. So far, all arsenic-sulfur species were synthesized or detected under reducing conditions, so, based on geochemical considerations, they are widely proposed to be monomeric (*11*−*13*, *16*) or polymeric (*16*−*21*) (reduced) thioarsenites. One recent paper reports them as thioarsenates (*14*) based on a literature review of early laboratory experiments (*22*, *23*) where arsenite oxidation in sulfidic solutions is explained by addition of sulfur to the nonbonding electron pair of arsenite. Absorption spectra and As−S-bonding lengths obtained by X-ray absorption near-edge spectroscopy (XANES), e.g., during a study on thioarsenic complex formation in neutral to alkaline arsenic sulfide solution, are consistent with a formal oxidation state of +3 for arsenic in dissolved thioarsenic species (*13*). However, a recent study in our laboratory indicates that the species we determined by ion chromatography and electrospray mass-spectrometry (IC-ICP-MS, ES-MS) are rather thioarsenates than thioarsenites (*10*). Using electrospray high-resolution mass-spectrometry on synthesized thioarsenic standards, that study implied that the measured to theoretical m/z ratios and the fragmentation pattern observed with ES-MS-MS showed consistently better agreement assuming thioarsenates compared to thioarsenites; fractions collected from ion chromatography with known S:As ratios confirmed the identification of thioarsenates versus thioarsenites. For the present paper we will thus pursue the line of argumentation that the thioarsenic species identified are thioarsenates acknowledging that we face some possible instrumental limitations, such as oxidation potential in the electrospray process or reversible processes and decomposition during chromatographic separations.

Preserving arsenic species in sulfidic waters is a challenge, and inappropriate preservation (in addition to inadequate analytical methods) is a major reason the occurrence and importance of thioarsenic species was overlooked in many previous studies. Critical reviews on existing arsenic species preservation methods (*24*, *25*) show that the most common and successful approach combines filtration, addition of a reagent (HCl, H_2SO_4, EDTA) to prevent dissolved iron or manganese oxidation and/or precipitation, and elimination of photooxidation by storage in the dark. In sulfidic waters, however, decreasing pH can cause instantaneous precipitation of poorly crystalline As_2S_3 and an immediate loss of total dissolved arsenic as observed in an earlier study upon acidification of synthetic solutions with HCl or HNO_3 to pH 2 (*26*). Flash-freezing was proposed in the mid 1980s as an alternative method for arsenite and arsenate stabilization (*27*). Freezing can promote formation of iron hydroxides, leading to oxidation, sorption, and coprecipitation of arsenic (*24*), and some reports, e.g. Daus et al. (*28*), showed significant loss of both arsenite and total dissolved arsenic after freezing. However, these samples were not flash-frozen but gradually frozen to −18 °C in a freezer. For sulfidic water samples, flash-freezing with liquid nitrogen at −196 °C has previously been shown to yield complete recovery of arsenic species

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with detection of a significant amount of thioarsenic species (*15*).

In this paper, results from a study on geothermal waters from Yellowstone National Park are used to (1) identify and quantify thioarsenates in sulfidic waters, (2) re-evaluate arsenic species preservation in such waters, and (3) investigate the importance of thioarsenates in geothermal waters, including the correlation of thioarsenates to hydrochemical properties and constituents, and the fate of arsenic discharged from geothermal springs.

Materials and Methods

Sampling Locations. Samples were collected in June/July 2006 at 50 sites in the following geothermal areas within Yellowstone National Park: Nymph Lake (NL), Hazle Lake (HL), Ragged Hills (RH), Gibbon Geyser Basin (GG), and Lower Geyser Basin (LG) (Supporting Information (SI) part EA1). The sampling sites were selected based on previous hydrogeochemical data (*29*) to cover a wide range of pH, solution composition, and arsenic concentrations ranging from a few μg/L to more than 10 mg/L with sulfide concentrations from less than 10 μg/L to 4 mg/L.

Field Work. Samples were collected under minimal exposure to the atmosphere by a low-flow peristaltic pump connected to an all-polytetrafluorethylene (PTFE) filter unit with a 0.2-μm pore-size filter membrane. All sampling bottles were pre-cleaned with HNO_3, rinsed with deionized water in the laboratory, and pre-rinsed with filtered water prior to sample collection. Samples for arsenic speciation were flash-frozen on dry ice immediately after collection in 60-mL high-density polyethylene bottles without further preservation and stored frozen at −20 °C for 7 to 27 days prior to analysis. At five sampling sites (samples GG09, LG02, LG03, LG11, LG19), five replicate samples each were collected in separate bottles for a storage stability study. These samples were collected on the last day of field work, flash-frozen, and kept frozen at −20 °C until analysis 5, 8, 17, 24, and 69 days later. Sample collection and preservation for major ions and trace elements was conducted according to procedures described previously (*29*). Briefly, samples for anion determination by ion chromatography (IC) and dissolved organic carbon (DOC) determination were collected without preservation. Samples for trace-element determination by inductively coupled plasma atomic emission spectrometry (ICP-AES) were preserved on-site by adding 1% by volume of concentrated redistilled HNO_3. Samples for total arsenic determination by hydride-generation atomic absorption spectrometry (HG-AAS) were acidified by adding 1% by volume of 6 N redistilled HCl. Samples for thiosulfate (S_2O_3) determination were preserved by adding 1.7% by volume of 0.6 M Zn-acetate and 1% by volume of 1 M NaOH to prevent sulfide oxidation (*29*). The on-site parameters pH, conductivity, and redox potential were measured using a MultiLine P4 with a SenTix 97/T pH electrode, a TetraCon 325 conductivity cell, and a Pt 4805/S7 probe (WTW, Germany). Dissolved oxygen was measured with a HACH HQ20 luminescent dissolved oxygen sensor. To increase sensor long-term performance, samples were cooled to less than 50 °C using a 50 m PTFE hose coiled around an open aluminum tube for heat conduction. The redox-sensitive constituents sulfide, ferrous iron, and total dissolved iron were determined photometrically according to the HACH methylene blue (#8131), 1,10-phenanthroline (#8146), and FerroVer (#8008) methods, respectively. The reactions of the thioarsenates toward the HACH methylene blue method are still unclear. For the present purpose, the photometrically determined sulfide concentrations are interpreted to represent the free sulfide concentrations in the sample.

Analytical Methods. Determination of total arsenic by HG-AAS and ICP-AES and major constituents followed established procedures (*29*). Flash-frozen samples for arsenic speciation were thawed and handled exclusively in an oxygen-free atmosphere in a glove box prior to analysis by anion-exchange chromatography coupled to inductively coupled plasma mass-spectrometry (AEC-ICP-MS) using NaOH as the eluent (*10*, *11*; Table 1). For inorganic arsenic species, an anion suppressor was used postcolumn to electrochemically neutralize the hydroxide eluent and remove the counterion (Na^+), thus, reducing the salt load introduced into the plasma resulting in improved detection limits and better long-term stability. Since the removal also affects other cationic species, such as dimethylated arsenic, samples for which significant amounts of methylated arsenic species were suspected were re-run without the suppressor and using a slightly modified program with a less alkaline eluent (Table 1).

Simultaneous ICP-MS on-line detection of arsenic (as AsO^+, $m/z = 91$) and sulfur (as SO^+, $m/z = 48$) in eluting compounds was accomplished using the dynamic reaction cell (DRC) technology with O_2 as reaction gas (Table 1). Both the arsenic and sulfur trace can be monitored simultaneously and potential interferences from $ArCl^+$ ($m/z = 40 + 35 = 75$) on As^+ ($m/z = 75$) are eliminated, but the arsenic signal intensity in DRC mode under these conditions is about one-third lower than that in standard mode. Under these conditions the detection sensitivity for sulfur is 12−18% (on a molar basis) of the detection sensitivity for arsenic. Arsenite, arsenate, mono- and dimethylarsenate were quantified using standard solutions made from solids ($NaAsO_2$, J.T. Baker, Phillipsburg, NJ; Na_2HAsO_4, Sigma-Aldrich, Oakville, ON; $CH_3AsNa_2O_2{\cdot}6H_2O$, ChemService, West Chester, PA; $(CH_3)_2AsNaO_2{\cdot}3H_2O$ Sigma, St. Louis, MO). Due to the lack of pure standards, inorganic and methylated thioarsenates were quantified using the arsenate calibration curve, which is justified by the good arsenic speciation mass balance (see below), i.e., the match between the sum of all arsenic species and the independently determined total arsenic concentrations in a sample. Similarly, ammonium sulfate ($(NH_4)_2SO_4$, Fluka Sigma-Aldrich, Oakville, ON) was used to quantify the amount of sulfur in the thioarsenate species.

No water reference material is certified for arsenic species, let alone thioarsenates. Matrix duplicates and matrix spike duplicates analyzed with every sample batch showed excellent precision with mean and maximum standard deviations of 2.2% and 8% for all arsenic species (except for tetrathioarsenate, which was omitted because of infrequent detection at very low concentrations). Spiking selected samples with arsenite and arsenate yielded total arsenic recovery between 94% and 107%. In samples with high sulfide concentration, the spiked species were recovered intact in alkaline samples (pH 9) but in acidic samples (pH 2−4) arsenate recovery was low (85%), while arsenite and monothioarsenate were increased by 12% and 8%, respectively.

The sum of arsenic species determined by AEC-ICP-MS was compared to total arsenic determination in frozen samples by ICP-MS and ICP-AES, in HCl-stabilized samples by ICP-AES and HG-AAS, and in HNO_3-stabilized samples by ICP-MS, ICP-AES, and HG-AAS. Total arsenic results obtained from ICP-MS were corrected by an internal rhodium standard ($RhCl_3{\cdot}H_2O$, SCP Science, Bale d'Urfé, QC) to compensate for instrument sensitivity drift over long analytical runs. Measured concentrations of an analytical reference material (TM-DWS, Environment Canada, National Water Research Institute) were 104% ± 2.6% of the certified total arsenic concentration. Matrix spikes were recovered quantitatively (mean 106% ± 1.2%) and reproducibility of matrix duplicates was excellent (mean 0.4%, maximum 1.6%).

Molecular mass spectra for thioarsenates were obtained with an electrospray triple quadrupole/linear ion trap mass spectrometer (Table 1).

TABLE 1. Instrumental Parameters for Determination of Arsenic Oxy- and Thioanions by AEC-ICP-MS AND ES-MS

	AEC Separation	
column	**IonPac AS-16/AG-16 4-mm (10−32) (Dionex, Sunnyvale, CA)**	
eluent	**NaOH (0.1 mol/L) at 1.2 mL/min**	
gradient	inorganic species (suppressor): 0−7 min 20 mmol/L 7 → 17 min 20 → 100 mmol/L 17−25 min 100 mmol/L 25−28 min 20 mmol/L	plus methylated species (no suppressor): 0−3 min 2.5 mmol/L 3 → 5 min 2.5 → 20 mmol/L 5−10 min 20 mmol/L 10 → 20 min 20 → 100 mmol/L 20−24 min 2.5 mmol/L
sample volume	depending on total arsenic concentration: 6−100 μL	
typical retention times	inorganic species (suppressor): arsenite: 171 ± 2 s (n = 37) arsenate: 705 ± 7 s (n = 37) monothioarsenate: 818 ± 2 s (n = 30) dithioarsenate: 922 ± 2 s (n = 28) trithioarsenate: 1024 ± 2 s (n = 27) tetrathioarsenate: 1104 ± 4 s (n = 8)	plus methylated species (no suppressor): dimethylarsenate: 260 ± 3 s (n = 12) dimethylmonothioarsenate: 358 ± 3 s (n = 8) arsenite: 405 ± 3 s (n = 28) monomethylarsenate: 550 ± 2 s (n = 9) monomethylmonothioarsenate: 643 ± 1 s (n = 5) arsenate: 948 ± 2 (n = 28) monothioarsenate 1039 ± 21 (n = 24) dithioarsenate 1134 ± 2 (n = 20)
suppression	ASRS-Ultra 4-mm (Dionex, Sunnyvale, CA), 300 mA current, 5 mL/min water (external mode)	
	ICP-MS detection	
instrument	Elan DRC II (PerkinElmer, Shelton, CT)	
plasma RF power	1300−1350 W	
nebulizer gas flow rate	1.00−1.04 L/min	
nebulizer	TR-30-C3 (Meinhard, Santa Ana, CA)	
spray chamber	cyclonic (Glass Expansion, Hawthorn East, Victoria, Australia)	
DRC reaction gas	O_2 flow rate 0.75 mL/min	
DRC settings	Rpa = 0; Rpq = 0.6 (AsO), 0.3 (SO)	
dwell times	species: m/z = 91 (AsO^+) 500 ms m/z = 48 ($32SO^+$) 500 ms	totals: m/z = 91 (AsO^+) 200 ms m/z = 103 (Rh) 200 ms m/z = 50 ($34SO^+$) 100 ms
	ES-MS-MS detection	
instrument	Q TRAP MS/MS (Applied Biosystems/MDS Sciex, Foster City, CA)	
flow rate	25 μL/min	
curtain gas	20.0 (arbitrary units)	
ion-spray voltage	−3500/-4000/-3500 V for mono-/di-/trithioarsenate	
ion-source gas	30/26/30 mL/min for mono-/di-/trithioarsenate	
declustering potential	−55/-45 /-35 V for mono-/di-/trithioarsenate	
entrance potential	−7/-4/-6 V for mono-/di-/trithioarsenate	
collision energy	−20 eV	
collision gas	high	
fixed fill time	20 ms	
scan rate	4000 amu/s	

Results and Discussion

Thioarsenate Identification. Mono-, di-, tri-, and tetrathioarsenic species have been previously synthesized in our laboratory, their S:As ratios were determined (1:1, 2:1, 3:1, and 4:1), and their identities as the respective thioarsenates were confirmed by electrospray mass-spectrometry (*10*; subject to the instrumental limitations of potential oxidation and decomposition as discussed in the introduction). In the 50 samples taken from Yellowstone geothermal waters, four arsenic species were detected besides arsenite and arsenate that match the retention times of these synthetic thioarsenate standards (SI part EA2, for general chemistry SI part EA3). We thus call them "thioarsenates" in the following discussion, acknowledging that the discussion about thioarsenates versus thioarsenites still remains controversial. Figure 1 shows an example of one of the chromatograms; typical retention times are given in Table 1.

In a previous study, S:As ratios of thioarsenates could not be determined in natural samples due to necessary dilution and a high number and concentration of overlapping sulfur species (*10*). Using the improved ICP-MS detection with DRC presented here, we were able to measure S:As ratios of mono-, di-, and trithioarsenate in geothermal samples accurately. The obtained results 0.95 ± 0.10 (n = 17), 1.92 ± 0.14 (n = 21), and 2.99 ± 0.22 (n = 26), matched the expected ratios of 1, 2, and 3 very well (SI part EA4). Tetrathioarsenate was detected in only eight samples at very low concentrations, so the confirmation of its S:As ratio was unsuccessful because of insufficient S concentration (n = 3) or overlapping sulfur species (n = 5), leading to impossibly high S:As ratios (16−43; Figure 1). Even though mono-, di-, and trithioarsenate were detected in more samples (49, 41, and 30, respectively),

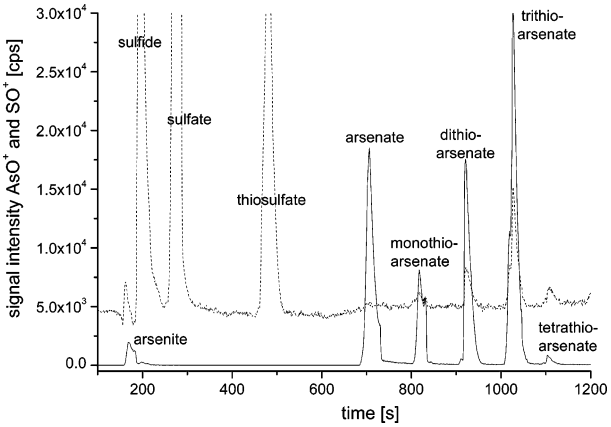

FIGURE 1. Chromatogram of an alkaline (pH 9, 90 °C) geothermal water (sample LG02) with high sulfide concentrations (3.7 mg/L) and a predominance of thioarsenates (solid line = AsO^+, dashed line = SO^+).

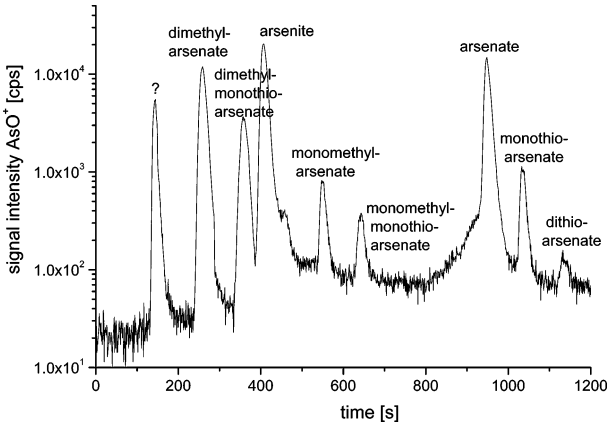

FIGURE 2. A few samples showed a substantial fraction of mono- and dimethylarsenate as well as a minor fraction of mono- and dimethylmonothioarsenate in addition to arsenite, arsenate, and the inorganic thioarsenates (sample HL02); the question mark indicates a peak of either an unidentified anionic arsenic species with a very short retention time or possibly an arsenic species in the dead volume.

some peaks had to be excluded from the S:As ratio calculations for the same reasons, especially for monothioarsenate (samples LG02 and LG07 in SI part EA4).

Molecular mass spectra determined by ES-MS-MS in two undiluted geothermal samples with the highest concentrations of monothioarsenate (sample RH02) and dithioarsenate (sample LG11) confirmed the presence of these two species. Distinct signals for m/z 157 (sample RH02) and m/z 173 (sample LG11), respectively, were observed, representing the molecular ions $H_2AsSO_3^-$ and $H_2AsS_2O_2^-$. Their fragment spectra showed signals resulting from elimination of H_2O and H_2S (m/z 139 and 123 for monothioarsenate, m/z 155 and 139 for dithioarsenate) comparable in relative intensity to synthetic standards (*10*). Although trithioarsenate was determined in many samples during the initial AEC-ICP-MS analyses, by the time the ES-MS-MS analyses were conducted, there was no longer a measurable signal for m/z 189. Tetrathioarsenate concentrations were too low to yield useful ES-MS-MS-spectra.

When all occurring arsenic species were included, the arsenic speciation mass balance was complete (mean ratio sum of species to total arsenic = 101% ± 10%, $n = 50$). For the few samples in which arsenic speciation mass balance was poor when only arsenite, arsenate, and thioarsenates were considered, we were able to confirm the presence of substantial amounts of methylated arsenic species using a different chromatographic separation (Table 1). The two samples from Hazle Lake (samples HL01, HL02), a geothermal-influenced wetland, and one sample from Frying Pan Spring (sample NL02) showed a large fraction of dimethylarsenate (13−19%) besides 1% monomethylarsenate. We were also able to detect traces of dimethylmonothioarsenate (5.5% in samples HL02 and NL02) and monomethylmonothioarsenate (0.5% in samples HL01, HL02, NL02) (Figure 2), as identified by previously synthesized standards (*30*). Note: Because of a different chromatographic separation (conditions see Table 1) retention times differ from those in Figure 1

This agreement is excellent considering that the sum of arsenic species is affected by analytical precision and uncertainties of peak integration for generally five and in some cases, such as samples HL02 or NL02, up to eight species. Few samples with initially low species mass balance (e.g., samples GG01 89%, RH02 71%, RH11 83%) showed better agreement with total arsenic when reanalyzed after 2 months (samples GG01 95%, RH02 106%, RH11 95%), however, at the expense of species conversion. The initially low total arsenic concentrations may be explained by formation and redissolution of colloids and/or sorption and redissolution of arsenic during freezing and thawing. Overall, bivariate nonparametric correlation analysis showed no significant correlation between the ratio (sum of species/total arsenic concentrations) and any other constituent, suggesting that major matrix constituents caused no significant systematic bias, e.g., by adsorption (iron and manganese hydroxides) or chromatographic competition (major anions).

The excellent arsenic mass balance also excludes the presence of other thioarsenic species in significant concentrations. Particularly, no evidence for the existence of the three monomeric thioarsenites postulated to form in anaerobic sulfidic environments (*11*−*13*) was found. Their existence in high concentrations could only be masked if they showed exactly the same chromatographic behavior as the respective thioarsenates. Furthermore, we found no analytical evidence of significant amounts of polymeric arsenic-sulfur species at the time and temperature of analysis. These findings match previous experiments with synthetic samples where identical species were detected in undersaturated and near-saturated solutions (*11*). However, the possibility of an analytical artifact (e.g., dilution and monomerization during chromatographic separation) can currently not be ruled out.

Evaluation of Preservation Conditions. Acidifying sulfidic solutions either with HCl or HNO_3 has previously been reported to lead to instantaneous precipitation of poorly crystalline As_2S_3 and an initial loss of total dissolved arsenic. Over a period of 5 weeks total arsenic concentrations increased steadily until complete arsenic recovery was observed (*26*). By analyzing HNO_3-preserved samples stored 2−8 weeks in transparent polyethylene bottles we did not observe any significant total arsenic loss and found good agreement with total arsenic concentrations in the frozen samples (106% ± 13%, SI part EA5). For HCl-preserved samples, analyzed 4−6 weeks after sampling, we detected low mean recovery rates of only 68% for total dissolved arsenic (SI part EA5). Minimum recoveries were as low as 11% (sample LG02) and 14% (sample GG08) for the two samples with the highest sulfide concentrations (3.70 and 3.95 mg/L, respectively). Using Spearman bivariate correlation analysis, the loss of arsenic in the HCl-acidified samples correlated directly with the sulfide and thioarsenate concentrations on a significance level of 1%. We conclude that HNO_3 may be more suitable than HCl for preserving total dissolved arsenic concentrations in sulfidic waters because of its potential for photooxidation (*24*) and should be considered in further research as an alternative to more elaborate procedures such as base addition followed by oxidation with H_2O_2 and acidification as suggested earlier (*26*). From the present study we cannot conclude whether HNO_3 addition prevents initial arsenic-sulfide precipitation or redissolves precipitated arsenic-sulfides within the first weeks of storage; results of a previous study seem to support the latter scenario (*26*). The fact that we obtained complete recovery of total arsenic after 2 instead of 5 weeks in the previous study (*26*) might be attributed to storage in transparent versus amber sampling bottles without exclusion of light. Addition of HCl, the most widely recommended method for arsenic species preservation (*24*), leads to precipitation of arsenic-sulfides and thus low total arsenic recovery rates even after up to 6 weeks of storage if the concentrations are high enough to reach arsenic-sulfide saturation. Any acidification is unsuitable to preserve arsenic speciation in sulfidic waters where thioarsenates are expected to play an important role.

Flash-freezing in dry ice was chosen as the best method for arsenic species preservation in the Yellowstone water samples. Low total arsenic recoveries of 39 and 47% were

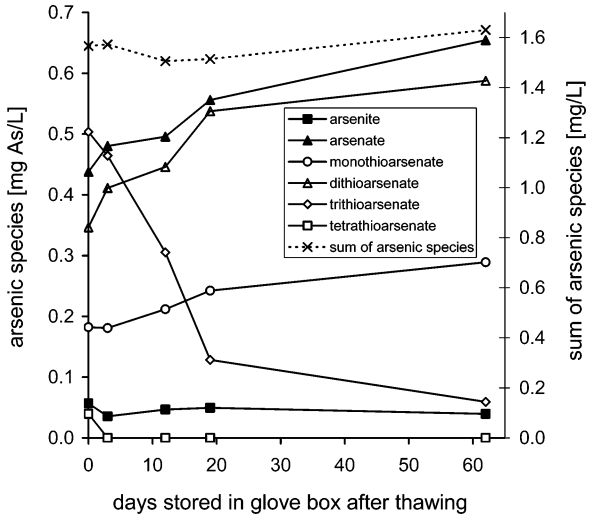

FIGURE 3. Experiments on stability of thioarsenates in a sample from Bath Spring (pH 9.0) after thawing show increase of thioarsenates with less SH-groups and decrease of total thioarsenate concentration; the sum of arsenic species (1.56 ± 0.05 mg/L, on the secondary *y*-axis) did not change during the experiment and compares very well with total arsenic determined in an independent sample (1.59 mg/L, data not shown).

observed in a previous study (*15*) using dry ice freezing at −78.5 °C compared to full recovery using liquid nitrogen freezing at −196 °C. In our study, flash-freezing with liquid nitrogen was not feasible because of the remote locations of some sampling sites and National Park safety regulations. However, the excellent total arsenic recovery rates confirm the suitability of dry ice for the present application. For a storage stability experiment, 5 replicates each were collected at 5 different sites with pH values between 6.4 and 9.1, frozen on dry ice, and stored in the freezer at −20 °C for 5, 8, 17, 24 and 67 days. Standard deviations for these time-series replicates (2−7% for arsenite, 1−4% for arsenate, 1−2% for monothioarsenate, 3−9% for dithioarsenate, and 6−13% for trithioarsenate) are in the range of the overall analytical precision, so there is no trend of thioarsenate species conversion or substantial total arsenic loss. Some variability may also be explained by formation and redissolution of colloids during freezing and thawing and different time lags between thawing and final analysis (5−18 h). Tetrathioarsenate was only present in two samples and was not detected anymore after day 5 (sample LG19) and day 17 (sample LG02).

Once thawed, samples stored at room temperature in the glove box showed a continuous decrease of trithioarsenate and an increase of di- and monothioarsenate over 3 weeks (Figure 3). Total thioarsenate concentrations also decreased. As in previous experiments (*10*) we detected arsenate as final end product in some samples (Figure 3) supposedly resulting from a ligand exchange reaction. In other samples we also observed transformation to arsenite. Tetrathioarsenate concentrations dropped to levels below detection limit within 3 days. Because 5 days was the minimum feasible transfer time from the field to the laboratory we have no means of accounting for transformations that may have occurred between sampling and first analysis after 5 days. The low concentrations of tetrathioarsenate might be a storage artifact. However, the high percentage of thioarsenates determined in some of the samples and the results of the stability tests between 5 and 67 days show that freezing is the best currently available technique for the preservation of arsenic species in sulfidic waters. Frozen storage duration should be kept to a minimum and samples must be analyzed immediately after thawing.

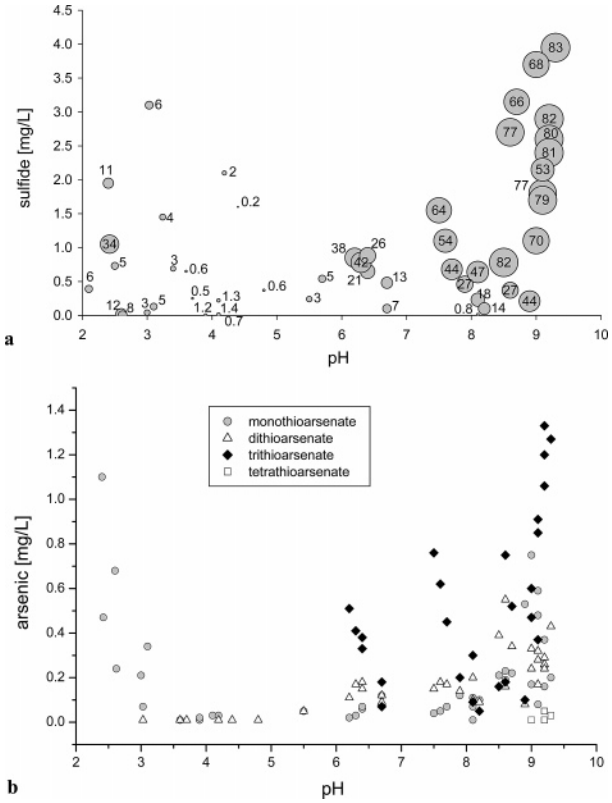

FIGURE 4. Sum of thioarsenates (percentage presented by dot size in panel a) determined in the geothermal waters relative to pH and sulfide concentrations, confirms the predicted predominance of thioarsenates, mainly trithioarsenate (panel b), under alkaline conditions. Up to 34% monothioarsenate was also found under acidic conditions (panel b).

Importance of Thioarsenates in Geothermal Waters. As mentioned before, thioarsenates were detected at all 50 sites sampled. The sum of thioarsenates dominated arsenic speciation in one-third of all samples with a maximum fraction of 83% (Figure 4a). Bivariate correlation analyses confirmed that the highest total thioarsenate concentrations correlated with high source temperatures, low redox potentials, low concentrations of dissolved oxygen, high sulfide, and low thiosulfate concentrations, as well as high pH, in accordance with previous reports (*10*−*14*; for chemistry data, see SI part EA3). The low tetrathioarsenate concentrations detected are consistent with earlier observations that its stability range is pH 10−13 (*31*), which is more alkaline than any of the sampled geothermal waters. Trithioarsenate was predominant in 10 samples, mono- and dithioarsenate were predominant in one sample each. The predominance of a trithioarsenic species is consistent with previous findings in near-neutral to alkaline sulfidic waters (*11*, *14*, *15*) [Note that while both refs *11* and *15* used the same chromatographic separation as in the present paper and refer to the same species, it is not named "trithioarsenate" but "trithioarsenite" (*11*) and "trithioarsenic species" (*15*) owing to the current controversy on thioarsenates versus thioarsenites as outlined in the introduction]. Trithioarsenate was not detected below pH 6 (Figure 4b), although earlier observations suggest it might only precipitate below pH 5 (*31*). Dithioarsenate was detected in small amounts under acidic conditions, but increased with increasing pH. Very interesting is the distribution of monothioarsenate with high concentrations both at very alkaline (pH 9) and acidic (pH 2.5) conditions. The highest fraction of thioarsenates under acidic conditions was 34% (all monothioarsenate) in a sample with pH 2.4 (sample RH11). Thioarsenic species so far have only been found in

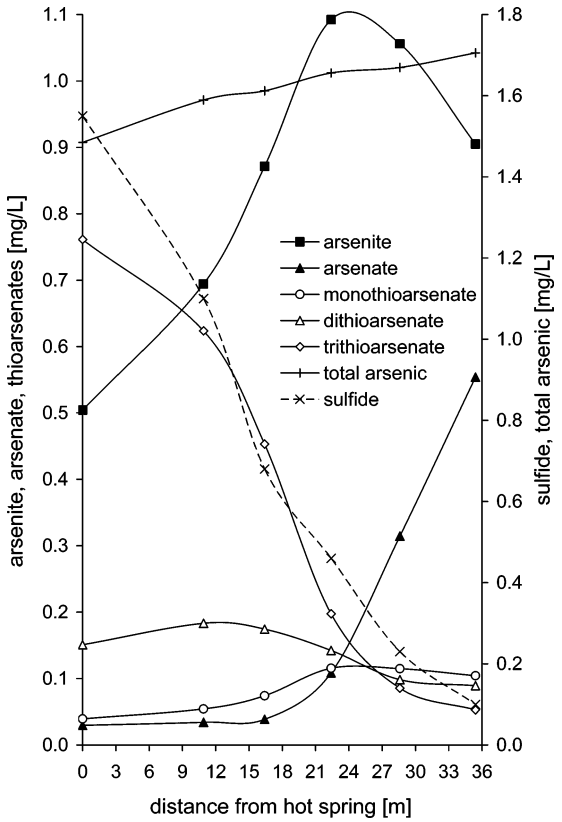

FIGURE 5. Arsenic speciation transect along the drainage channel of the hot spring Ojo Caliente shows quantitative transformation of trithioarsenate to arsenite; ligand exchange from tri- via di- and monothioarsenate to arsenate constitutes a minor reaction; oxidation of arsenite to arsenate only becomes quantitatively important after thioarsenates have disappeared (pH increased from 7.5 to 8.6).

waters with near-neutral to alkaline pH (*10*−*15*). This is the first report on significant natural thioarsenate occurrence under acidic conditions.

With thioarsenates occurring in all samples, and dominating arsenic speciation in one-third of them, the previous concept of geothermal arsenic chemistry involving only arsenite and arsenate (*7*) requires revision. One consequence of this is that the fate of arsenic discharged from geothermal springs can no longer be conceptualized as a simple oxidation reaction from arsenite to arsenate in the drainage channels. To obtain a first impression of the processes occurring in such environments, one transect with six sites was sampled along the drainage channels of the hot spring Ojo Caliente (samples LG03−LG08). Ojo Caliente had been studied in this regard twice previously (*29*), but arsenic speciation was determined using the conventional hydride-generation atomic absorption spectrometry which does not differentiate the thioarsenates. Those studies demonstrated the expected predominance of arsenite at the source of the hot spring, which was converted rapidly to arsenate at some point along the transect (*7*). Our study shows a different arsenic speciation profile along the drainage channel (Figure 5), including the presence of thioarsenates up to significant distances from the source.

Trithioarsenate predominates at the hot spring's source (51% of total arsenic) and is converted to arsenite (53%) and arsenate (33%) at the end of the drainage channel. A minor reaction is the stepwise ligand exchange of SH^- by OH^- groups reflected by a successive increase of first dithioarsenate (maximum at 12−14 m), then monothioarsenate (maximum at 24−26 m). The end product of this reaction pathway is arsenate. The quantitatively major reaction, however, is the transformation from trithioarsenate to arsenite within the first 24 m from the source. No other intermediate species are found to form in substantial concentrations during that time, which is confirmed by the arsenic mass balance. Oxidation of arsenite to arsenate, the previously assumed predominant mechanism in the drainage channels, only becomes quantitatively important after all thioarsenates are converted. With the current limited knowledge on the behavior of thioarsenic species in the environment and the controversy of thioarsenate versus thioarsenite identification it is premature to propose a balanced reaction for the processes occurring in the drainage channel. If our identification of thioarsenates is wrong and thioarsenites predominate instead of thioarsenates, their transformation to arsenite would present a ligand exchange SH^- versus OH^-. Presuming our identification of thioarsenates is correct, their detection under relative reducing conditions requires the presence of S^0-donors such as polysulfides, thiosulfate, and polythionates oxidizing arsenite (*32*). Apart from our analytical evidence for the presence of thioarsenates, the presence of polysulfides is indicated by speciation calculations and thiosulfate was detected at the geothermal source (0.6 mg/L) (*33*).

The present study showed that thioarsenic species are key species in redox reactions between arsenite and arsenate in sulfidic aquatic systems. Their significance in the environment further underlines the necessity for unambiguous structural identification (thioarsenates versus thioarsenites) so that in the future balanced reactions can be provided for arsenic redox processes in sulfidic aquatic systems.

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Supporting Information Available

Further information on sampling locations in Yellowstone National Park, their basic water chemistry and arsenic speciation data, including calculation of S:As ratios and comparison of arsenic preservation using different methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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