Speciation of arsenic in sulfidic waters

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Formation constants for thioarsenite species have been determined in dilute solutions at 25 °C, ΣH2S from 10–7.5 to 10–3.0 M, ΣAs from 10–3.6 to 10–4.8 M, and pH 7 and 10. The principal inorganic arsenic species in anoxic aquatic systems are arsenite, As(OH)3, and a mononuclear thioarsenite with an S/As ratio of 3 : 1. Thioarsenic species with S/As ratios of 1 : 1, 2 : 1, and 4 : 1 are lesser components in sulfidic solutions that might be encountered in natural aquatic environments. Thioarsenites dominate arsenic speciation at sulfate concentrations > 10–3.3 M at neutral pH. Conversion from neutral As(OH)3 to anionic thioarsenite species may regulate the transport and fate of arsenic in sulfate-reducing environments by governing sorption and mineral precipitation reactions.

1. Introduction

The chemical speciation of arsenic in natural waters determines its reactivity, toxicity, and transport in the environment.1–4 Historically, the formation of soluble thioarsenic species has been recognized as an important factor governing arsenic chemistry in reducing environments.5–17 This observation has been paralleled by efforts to identify and quantify the chemistry controlling the formation of thioarsenic species in nature, yet reliable analytical strategies for these species are not fully developed.18 Speciation models derived from thermodynamic analysis of arsenic sulfide solubility in aqueous systems support the existence of thioarsenite species,9,12–15 as do more recent molecular orbital theory calculations and Raman spectroscopic data.16,17,19 Despite these extensive efforts, available data are limited for many practical applications because they provide an indirect quantification of thioarsenite stability and stoichiometry at conditions that are often unrepresentative of aquatic environments, i.e., at saturation with respect to an arsenic sulfide. Excluding some low-pH environments,20 natural systems are usually found to be highly undersaturated with respect to arsenic sulfides such as orpiment.21,22 Development of thermodynamic data for mineral and aqueous species is critical towards assessment of arsenic chemistry in sulfate-reducing environments. This geochemical setting is commonly encountered in organic-rich surface and groundwater systems, e.g., landfill leachate plumes,23 hydrocarbon contaminant plumes,24 and lucustrine to marine systems.25,26

In this paper, we provide new experimental data that explore arsenic speciation in sulfidic waters and examine the results of previous solubility studies in light of the new experimental evidence. Reported herein is a direct analytical quantification of thioarsenite species formed under environmentally relevant conditions.

2. Experimental

In order to make accurate predictions of arsenic mobility in reducing natural systems, an understanding is needed of the stoichiometry and stability of dissolved arsenic species in sulfide-deficient and sulfide-bearing solutions. We examined the change in As(III) speciation from arsenite to a distribution of thioarsenic species with increasing sulfide concentrations in aqueous solution. The switch in arsenic speciation from oxyanionic to sulfonxyanionic forms was reversible and triggered by adding aliquots of a 1 mM sodium bisulfide buffer to solutions containing about 2 to 15 μM arsenite from NaAsO2. The concentrations of arsenite and individual thioarsenic species were determined by ion chromatography–inductively coupled plasma–mass spectrometry (IC-ICP-MS).

Solutions were prepared at nominal pH values of 7 and 10 with ΣH2S/ΣAs ranging from 0.002 to 350 on a molar basis. Actual pH values varied by as much as 0.8 units from the nominal values. Experimental conditions were selected to be undersaturated with respect to amorphous As2S3. Based upon Eary’s solubility model for amorphous As2S3, arsenic concentrations were between 0.02 and 50% of saturation at pH 7 (Fig. 1a). At pH 10, solutions were highly undersaturated with respect to amorphous As2S3; total arsenic concentrations were always less than 0.1% of those expected at saturation (Fig. 1b).

All solutions were prepared using deoxygenated and distilled water (Milli-Q 18 MQ). Removal of dissolved oxygen to concentrations < 0.2 mg L–1 was verified by using rhodamine D colorimetric test kits (Chemetics, K-7501). Sodium bisulfide solutions were prepared by purging dilute oxygen-free sodium hydroxide solution with high-purity 1% (v/v) hydrogen sulfide gas. The resulting buffer solution had a pH of 7.0 and a ΣH2S concentration of 1.1 mM. In all cases, bisulfide solutions were used within 12 h of preparation. Arsenite solutions were prepared by dissolving quantities of NaAsO2 (Fisher Reagent Grade) into nitrogen-purged water.

Arsenic and bisulfide solutions were mixed and sealed in 45 mL glass reaction vessels within an anaerobic glove box and allowed to equilibrate for 1 to 4 h. After this time period, solutions were flash-frozen in liquid nitrogen and kept frozen until analysis to insure species preservation. Experiments were conducted at pH 7 (± 0.3) and pH 10 (± 0.8). In the high-pH experiments, pH was adjusted by adding aliquots of 0.01 M NaOH. All experiments were conducted at room temperature (23 ± 1.5 °C). Reversibility was tested by spiking solutions with arsenite immediately prior to analysis and tracking the re-equilibration of arsenic speciation. The results of these tests indicated that rates of equilibration are rapid among the oxyanion and thiooxyanions of arsenic in sulfidic solutions.
Arsenic speciation was determined by ion chromatography coupled on-line to inductively-coupled plasma mass spectrometry (IC-ICP-MS). Chromatographic separation was achieved for 1 mL samples using gradient elution with dilute NaOH on a high-capacity anion exchange column, similar to a method previously used for selenium speciation in natural waters. A DX-500 ion chromatograph (Dionex) and an Elan 6000 ICP-MS (Perkin Elmer) were used for these experiments. Arsenic and sulfur were simultaneously detected by monitoring the mlz = 75 (As) and 48 (SO) signals, and quantified based on peak area. From the obtained signals, the As/S ratios for the separated thioarsenic species were calculated in each sample, and then averaged over all samples in which no apparent interferences on either signal were observed. At constant $\Sigma H_2S/2\Sigma As$, variations in sample pH yielded differing speciation trends, evidence that equilibration of the sample during chromatographic elution did not direct the outcome of the speciation results. The analytical method is described in detail in a forthcoming publication (Wallschläger et al., in prep.).

3. Results and discussion

Thioarsenite species

Experimental conditions and results are listed in Table 1. Results indicate that, in addition to arsenite, sulfidic solutions may contain up to four distinct thioarsenic species with average S/As ratios of 1 : 1, 2 : 1, 3 : 1, and 4 : 1 (Fig. 2, Table 2). The same species appear in solutions highly undersaturated with respect to amorphous $\text{As}_2\text{S}_3$ and in near-saturated solutions. Recovery of arsenic during analysis was in all cases between 96 and 102%, which indicates that there was no major loss of arsenic during chromatographic separation and that the principal arsenic species are accounted for in our analysis. At pH 7 and $\Sigma As = 10^{-4.9}$ M, the crossover from arsenite- to thioarsenic-dominated speciation occurred at $\Sigma H_2S$ of about $10^{-4.3}$ M. The crossover in arsenic speciation is in excellent correspondence with the $\Sigma H_2S$ concentration where the slope on a log [As] versus log $[\Sigma H_2S]$ solubility diagram transitions from a negative to a positive value (Fig. 1a). Eary proposed that the change in slope at higher total sulfide concentrations indicates a change in arsenic speciation from arsenite to thioarsenite, either the mononuclear 3 : 1 thioarsenite species ($\text{As}$(SH)$_3^+$), the trinuclear 2 : 1 species ($\text{As}$(SH)$_2$S), or their respective deprotonated forms. The results of this study suggest that in fact multiple species with S/As ratios ranging from 1 : 1 to 4 : 1 account for the solubility of opuntin in sulfidic solutions.

At pH 10, the observed crossover in arsenic speciation from oxyanionic to sulfoxynionic forms shifted to a slightly higher $\Sigma H_2S$ concentration of about $10^{-3.5}$ M. Based on the solubility model for amorphous $\text{As}_2\text{S}_3$, the crossover point at pH 10 is predicted to be $\Sigma H_2S = 10^{-2.5}$. However, it should be noted that the 25 °C $\text{As}_2\text{S}_3$ solubility determinations of Eary, Webster, and Mironova et al. were in all cases determined below pH 9, hence the solubility curve shown on Fig. 1a has been extrapolated outside of the measured range. Analysis of the isothermal pH and $\Sigma H_2S$-dependent solubility of crystalline and amorphous $\text{As}_2\text{S}_3$ represents the method most often used to determine the formation constants of thioarsenic species. Proposed arsenic species in sulfidic waters include mononuclear (e.g., $\text{As}_2\text{S}_3^-$), dinuclear (e.g., $\text{As}_2\text{S}_4^2-$), and trinuclear thioarsenites (e.g., $\text{H}_3\text{As}_2\text{S}_4$). Trimeric thioarsenite species have frequently been selected as the solubility-controlling species of disordered and crystalline opuntin in sulfidic solutions. However, as noted above solubility data for opuntin are consistent with the formation of either mononuclear 3 : 1 species, trinuclear 2 : 1 thioarsenite species, or both. Underlying thermodynamic analysis of mineral-buffered experiments in this system is complicated by the fact that the chemical potential of $\text{As}_2\text{S}_3$ is fixed by equilibration with a solid (opuntin); consequently, it is not possible to accurately distinguish between monomeric and polymeric species. In related studies, molecular orbital theory has been used to calculate bond distances, vibrational frequencies, gas-phase energetics, and proton affinities for various thioarsenite molecules to aid interpretation of EXAFS and Raman spectra of arsenic in concentrated 1 M NaHS solutions. Based on modeling results, the existence of dimeric thioarsenic species has been rejected in solutions saturated with $\text{As}_2\text{S}_3$ in favor of monomeric or trimeric species. In the context of the present study, the trends in chromatographic elution times (Fig. 2), the fact that the same series of thioarsenic species were observed in solutions ranging from highly undersaturated to near-saturated with respect to amorphous $\text{As}_2\text{S}_3$, and the dominance of the 3 : 1 complex are all consistent with the presence of mononuclear thioarsenic species at the conditions of our experiments ($\Sigma As$ from $10^{-5.6}$ to $10^{-4.9}$ M); conditions typical of groundwater and surface water environments. With increasing pH and $\Sigma H_2S$, arsenic concentrations at saturation with opuntin easily exceed $10^{-7}$ M; conditions where polynuclear species might be anticipated. The 4 : 1 thioarsenite compound observed at pH 7 and $\Sigma H_2S/2\Sigma As > 20$ is somewhat unexpected although this complex stoichiometry has been previously proposed. Arsenic(n) compounds are expected to involve 3 bonded atoms plus a
detected in experiments at pH 10 and not in weakly sulfidic and moderately alkaline conditions, which occurred in relatively reducing solutions at near-neutral pH. A change in arsenic speciation at pH 7 from arsenite- to thioarsenite-dominated with increasing pH.

**Table 1 Experimental conditions and results**

| Exp. | pH  | log $\Sigma H_2 S$ | log $\Sigma As$ | As(n) | As(v) | S : As 1 : 1 | S : As 2 : 1 | S : As 3 : 1 | S : As 4 : 1 |
|------|-----|-------------------|----------------|-------|-------|-------------|-------------|-------------|-------------|
| 1    | 7.24| -7.51             | -4.82          | 0.998 | 0.002 | 0.000       | 0.000       | 0.000       | 0.000       |
| 2    | 7.30| -5.49             | -4.87          | 0.988 | 0.005 | 0.001       | 0.005       | 0.002       | 0.002       |
| 3    | 7.20| -4.96             | -4.87          | 0.917 | 0.015 | 0.012       | 0.032       | 0.024       | 0.000       |
| 4    | 7.01| -4.28             | -4.93          | 0.102 | 0.011 | 0.005       | 0.072       | 0.811       | 0.000       |
| 5    | 7.20| -3.85             | -4.90          | 0.007 | 0.001 | 0.001       | 0.027       | 0.962       | 0.003       |
| 6    | 7.12| -3.51             | -4.91          | 0.009 | 0.002 | 0.007       | 0.139       | 0.838       | 0.005       |
| 7    | 7.04| -3.49             | -4.91          | 0.011 | 0.003 | 0.004       | 0.094       | 0.865       | 0.023       |
| 8    | 7.17| -2.97             | -4.85          | 0.000 | 0.004 | 0.000       | 0.063       | 0.847       | 0.086       |
| 9    | 7.16| -3.50             | -5.63          | 0.000 | 0.004 | 0.004       | 0.078       | 0.902       | 0.012       |
| 10   | 7.00| -3.00             | -5.55          | 0.000 | 0.012 | 0.000       | 0.125       | 0.805       | 0.053       |
| 11   | 6.79| -5.96             | -4.85          | 0.994 | 0.010 | 0.000       | 0.000       | 0.000       | 0.000       |
| 12   | 7.24| -5.47             | -4.88          | 0.973 | 0.016 | 0.002       | 0.004       | 0.000       | 0.000       |
| 13   | 7.05| -4.96             | -4.87          | 0.960 | 0.005 | 0.014       | 0.021       | 0.000       | 0.000       |
| 14   | 7.20| -4.66             | -4.91          | 0.896 | 0.011 | 0.038       | 0.054       | 0.001       | 0.000       |
| 15   | 7.30| -4.48             | -4.94          | 0.748 | 0.030 | 0.026       | 0.089       | 0.955       | 0.000       |
| 16   | 9.13| -5.73             | -4.88          | 0.942 | 0.033 | 0.012       | 0.005       | 0.009       | 0.000       |
| 17   | 10.02| -4.99             | -4.94          | 0.840 | 0.000 | 0.114       | 0.045       | 0.003       | 0.000       |
| 18   | 9.83| -4.48             | -4.89          | 0.650 | 0.132 | 0.127       | 0.185       | 0.009       | 0.000       |
| 19   | 9.80| -3.80             | -4.89          | 0.290 | 0.035 | 0.024       | 0.198       | 0.454       | 0.000       |
| 20   | 10.90| -3.57             | -4.86          | 0.054 | 0.034 | 0.041       | 0.251       | 0.620       | 0.000       |
| 21   | 9.51| -4.54             | -4.96          | 0.800 | 0.000 | 0.124       | 0.063       | 0.005       | 0.000       |
| 22   | 9.67| -4.24             | -4.87          | 0.710 | 0.000 | 0.200       | 0.090       | 0.000       | 0.000       |
| 23   | 9.20| -3.96             | -4.94          | 0.470 | 0.050 | 0.071       | 0.221       | 0.184       | 0.000       |

*Concentrations in M. Concentrations of $\Sigma H_2 S$ were calculated based on gravimetric mixing ratios of the stock NaH$_2$S and arsenic solutions, and the measured thioarsenite speciation. $\Sigma H_2 S$ concentration in the stock NaH$_2$S solution was determined from the average of quadruplicate analyses using the methylene blue colorimetric method. Concentrations of $\Sigma As$ were determined by inductively coupled plasma–optical emission spectroscopy on unacidified samples. Precision of measurements: pH ~ 0.03; $\Sigma H_2 S$ ~ 5%; $\Sigma As$ ~ 5%; species fractional abundance (~5%) for F > 0.1, ~10% for 0.1 > F > 0.01, ~20% for F < 0.01.

**Table 2 Elution times and concentrations of arsenic and co-eluted sulfur in model solutions with $\Sigma H_2 S/\Sigma As$ = 0.8 (Exp. 3) and $\Sigma H_2 S/\Sigma As$ = 26 (Exp. 7)**

| Exp. | Species | Elution time/s | Arsenic/µmol L$^{-1}$ | Sulfur/µmol L$^{-1}$ | Molar ratio (S/As)$^b$ |
|------|---------|----------------|----------------------|----------------------|------------------------|
| 3    | Arsenite | 217           | 12.3                 | n.d.                 | –                      |
|      | Arsenate | 827           | 0.20                 | n.d.                 | –                      |
|      | S–As (1 : 1) | 922          | 0.17                 | 10.0                 | 0.009                  |
|      | S–As (2 : 1) | 1024         | 0.04                 | 10.0                 | 0.009                  |
|      | S–As (3 : 1) | 1129         | 0.12                 | 10.0                 | 0.009                  |
|      | S–As (4 : 1) | –            | n.d.                 | n.d.                 | –                      |
| 7    | Arsenite | 231           | 0.14                 | n.d.                 | –                      |
|      | Arsenate | 815           | 0.04                 | n.d.                 | –                      |
|      | S–As (1 : 1) | 914          | 0.05                 | 10.1                 | 0.009                  |
|      | S–As (2 : 1) | 1016         | 1.16                 | 10.1                 | 0.009                  |
|      | S–As (3 : 1) | 1119         | 10.6                 | 10.1                 | 0.009                  |
|      | S–As (4 : 1) | 1205         | 0.28                 | 10.9                 | 0.009                  |

*Among all samples variability of molar S/As ratios for the 2 : 1, 3 : 1, and the 4 : 1 complexes was 2.1 ± 0.3, 3.1 ± 0.7, and 4.2 ± 0.3, respectively. The first S–As complex is likely to be a 1 : 1 complex but in most cases the sulfur from this thioarsenate species co-eluted with sulfur from other sulfur species. This was evidenced by non-coincident retention times for As and S peaks. n.d., not detected.

**Fig. 2** Mass spectral chromatograms of mass 75(As) showing the change in arsenic speciation at pH 7 from arsenite- to thioarsenite-dominated with increasing $\Sigma H_2 S/\Sigma As$.

Sulfur and polysulfides through reduction of arsenate and speciation in sulfidic systems, either as an oxyanion or as a thioarsenate. Greater arsenate fractional abundance was found in the pH 10 experiments (0.032 ± 0.045, n = 8) as compared to the pH 7 experiments (0.009 ± 0.008, n = 15).

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This suggests that arsenate was likely an oxidation product of arsenite and we suspect that most arsenate production occurred during chromatographic separation.

At each sulfide concentration investigated, the species distribution of arsenic may be defined as the sum of all arsenic(III) species present in solution:

\[
\Sigma \text{As} = \Sigma \text{As(OH)}_3 + \Sigma \text{As(OH)}_2\text{SH} + \Sigma \text{As(OH)}_2\text{S} + \Sigma \text{As(OH)}\text{S} + \Sigma \text{As(OH)}\text{S}_2 + \Sigma \text{As(OH)}\text{S}_3 + \Sigma \text{As(OH)}\text{O}_2\text{S}_3
\]

As noted above, chromatographic results combined with the calculated degree of saturation are most consistent with the presence of mononuclear thioarsenic species. Multiple protonation states are possible for thioarsenites and it is expected that the acidity of thioarsenite species increases with progressive loss of anionic charges. The results of this study suggest that the solubility of amorphous or crystalline As$_2$S$_3$ in sulfidic waters is controlled by at least four thioarsenite species, each with multiple protonation states. Additional solubility expressions are possible for amorphous As$_2$S$_3$:

\[0.5\text{As}_2\text{S}_3 (am) + 2\text{H}_2\text{O} \rightleftharpoons \text{As(OH)}_2\text{S}^- + 0.5\text{HS}^- + 1.5\text{H}^+\]

\[0.5\text{As}_2\text{S}_3 (am) + 0.5\text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{As(OH)}_2\text{S}^- + 1.5\text{H}^+\]

\[0.5\text{As}_2\text{S}_3 (am) + 1.5\text{HS}^- \rightleftharpoons \text{As}_4\text{H}^+ + 0.5\text{H}^+\]

\[0.5\text{As}_2\text{S}_3 (am) + 2.5\text{HS}^- + 1.5\text{H}^+ \rightleftharpoons \text{As(SH)}_4^-\]

Table 4 Equilibrium constants for thioarsenite species

| Reaction | \[\log K \] | 25°C | I = 0 |
|---------|-----------|------|-----|
| As(OH)$_3$ + HS$^-$ + H$^+$ | 6.89 ± 0.29 | (n = 10) |
| As(OH)$_2$SH + H$_2$O | 3.54 ± 0.36 | (n = 8) |
| As(OH)$_2$S + HS$^-$ + H$_2$O | 5.06 ± 0.49 | (n = 17) |
| As(OH)$_2$S$^+$ + HS$^-$ + H$^+$ | 11.78 ± 0.89 | (n = 11) |
| As(SH)$_3$ + HS$^-$ + H$_2$O | 3.89 ± 0.41 | (n = 6) |
| As(SH)$_3$ + 2H$^+$ | 16.16 ± 0.29 | (n = 6) |

*Results are mean values ± standard error (2σ) determined from the fractional abundance of arsenite and thioarsenites in model solutions. Activity coefficients for charged species were estimated using the Davies equation.
with $\Delta G^0$ for As(OH)$_3^0$ of $-639.8$ kJ mol$^{-1}$, $\Delta G^0$ for HS$^-$ of $12.05$ kJ mol$^{-1}$, $\Delta G^0$ for H$_2$O(l) of $-237.18$ kJ mol$^{-1}$ (ref. 29), and $\Delta G^0$ for As$_2$S$_3$ (am) of $-75.94$ kJ mol$^{-1}$, based on the reaction:

$$0.5\text{As}_2\text{S}_3\text{(am)} + 3\text{H}_2\text{O} \rightleftharpoons \text{As(OH)}_3^0 + 1.5\text{HS}^- + 1.5\text{H}^+ \quad (6)$$

with $\log K_6 = -22.4$.\textsuperscript{15}

Estimated log $K$ values for reactions (2)–(5) are $-18.9 \pm 0.4$, $-13.8 \pm 0.5$, $-2.0 \pm 0.9$, and $14.1 \pm 0.3$, respectively. Arsenic solubility predicted by reactions (2)–(5) and (6) at pH 5 is plotted and compared in Fig. 4a to 25 °C solubility measurements reported in Eary.\textsuperscript{15} Visual inspection of Fig. 4a indicates that the 5-species model is in reasonable agreement with the solubility measurements as compared to the 2-species model shown in Fig. 4b. Note that no attempt was made to improve the fit to the orpiment solubility data and that data in Table 4 derived from experiments at pH 7 and 10 were extrapolated to pH 5. Fig. 4a was constructed using only reaction (6) and data that were derived from an independent set of measurements made in the absence of a solid phase. The calculated slope, $\Delta \log [\text{As}]/\Delta \log [\text{H}_2\text{S}]$, based on linear regression analysis of the solubility data with positive trend ranges from 1.75 to 1.91 depending on how the transition point is selected. In addition, regression analysis of amorphous $\text{As}_2\text{S}_3$ solubility data\textsuperscript{15} collected at 40 to 90 °C yields slopes that range from 1.64 to 2.15. These non-integer values are perhaps unlikely to be the result of a single thioarsenite species and may be the result of the presence of multiple thioarsenic species with varying S : As ratios in solutions saturated with $\text{As}_2\text{S}_3$. We suggest that because of the complexity of arsenic speciation in sulfidic solutions as indicated here and in previous studies,\textsuperscript{17} speciation analysis using direct methods is necessary to yield accurate speciation models from solubility measurements. Data sets provided in previous reports still provide detailed insight into total arsenic concentrations at saturation with crystalline and amorphous $\text{As}_2\text{S}_3$ and as such will continue to provide the basis for speciation studies.

**Thioarsenite species in the environment**

At near-neutral to mildly alkaline conditions the fractional abundance of arsenite relative to the sum of all thioarsenic species increases with increasing pH at a given $\Sigma\text{HS}_2$ concentration (Fig. 5a). This trend correlates with greater solubility of orpiment at near neutral to alkaline pH compared to low pH.\textsuperscript{12,14,15} Experimental results indicate that thioarsenite forms dominate over arsenite when sulfide concentrations are greater than about 0.1 to 1 mM. In general, concentrations of dissolved sulfide in aquatic systems are controlled by the rate of bacterial sulfate reduction and by the nature and

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Fig. 4 Experimental amorphous $\text{As}_2\text{S}_3$ solubilities at 25 °C from ref. 15 (squares) compared to predicted solubilities based upon (a) thioarsenite formation constants in Table 4 and selected thermodynamic constants (see text) and (b) the 2-species model, for example, as proposed in ref. 15.

Fig. 5 (a) Modeled fractional abundance of arsenite relative to thioarsenite species as a function of pH and sulfide concentration based on formation constants determined in this study (Table 4). (b) Predominance area diagram for aqueous arsenic species. The contours represent the activity of ferrous iron in equilibrium with mackinawite (FeS) at 25 °C.
abundance of iron in the solid matrix. Concentrations of dissolved sulfide are typically low when reactive iron is abundant, i.e., iron present in iron oxhydroxides, iron oxides, or Fe-bearing silicates. Dissolved sulfide concentrations are able to increase only after the supply of reactive iron is exhausted via reductive dissolution processes and subsequent iron monosulfide precipitation. Dissolved iron and sulfide are usually near saturation with respect to mackinawite (Fe₇S₈) or greigite (Fe₃S₄), and this relationship can be used to understand the conditions in which thioarsenites are expected to occur in natural environments (Fig. 5b). In solutions saturated with mackinawite over the pH range from 6 to 10, thioarsenites will dominate arsenic speciation only when dissolved ferrous iron concentrations are low (10⁻¹⁰ M to 10⁻⁶ M). In other words, the presence of reactive iron will generally preclude the formation of thioarsenic species in sulfide-reducing systems by maintaining low dissolved sulfide concentrations. Environments in which the abundance of reactive iron is limited will favor sulfide accumulation and thioarsenite formation.

The mobility of arsenic in aquatic systems is governed mainly by redox conditions. Arsenic sulfides, iron–arsenic sulfosalts, and iron oxides are believed to be the principal sources of arsenic to anaerobic ground waters through microbial and non-microbial processes. Based on the results of this study, dissolution reactions of arsenic-bearing materials should involve thioarsenite species in weakly to strongly sulfidic systems (Table 4; Fig. 5a). Although the eventual fate and distribution of thioarsenic species requires more investigation, these species are likely to be involved in adsorption, precipitation, and/or oxidation reactions. For example, precipitation of authigenic pyrite (FeS₂) is known to scavenge arsenic from solution. However, it is not clear if arsenic partitioning to pyrite is controlled by arsenite or by thioarsonite species. Precipitation of orpiment is another possible sink for thioarsenite in low pH environments. Orpiment has a molecular structure of linked pyramidal As₅S₉ units that are bound together by weaker chemical forces that give rise to the lack of hardness and low melting point of this mineral. Condensation of ΣAs(SH)₃, thioarsenide species, provides a reasonable pathway for nucleation and growth of orpiment.

Thioarsenite species may act as multi-dentate chelating agents that enhance the transport of highly-polarized (B-type) cations, such as Cu²⁺, Au⁺(n), Ag⁺, Tl⁺, and Hg²⁺. Copper concentrations in sulfidic wetland systems, in addition to concentrations of zinc and cadmium, are too high to be accounted for by the solubility of simple metal sulfides and investigations suggest that existing thermodynamic data are too incomplete to accurately describe the factors that govern metal mobility in sulfidic systems. Yet when solubility behavior in ternary systems has been studied, increases of several orders of magnitude in copper solubility can occur due to the formation of mixed Cu–thioarsenite species in the sulfide concentration range of 0.001 to 0.1 mM. Our limited understanding of ternary metal–As–S systems is significant considering the potential importance of such species for regulating contaminant transport and fate processes in natural systems and at hazardous waste sites. Furthermore, the association between the distributions of arsenic and gold in shallow hydrothermal deposits has long been recognized. Gold is often found in low-temperature (~<200 °C) sulfide deposits associated with arsenian pyrite, silver–arsenic sulfosalts, and as discrete arsenic sulfides. Solubility studies are needed in the ternary system Au–As–S to evaluate the possible role of gold transport by thioarsenic species. Results documented herein provide the basis for reliable and accurate determination of ternary metal–thioarsenite complexes.

4. Conclusions

Our study provides direct analytical confirmation of the complexity of the As–S–O–H system as indicated in previous studies. Monomeric thioarsenic species with S/As ratios of 1 : 1, 2 : 1, 3 : 1, and 4 : 1 were detected in model sulfidic solutions. Thioarsenites dominate arsenic speciation at sulfide concentrations > 10⁻⁴ M at neutral pH and results of this study suggest that thioarsenite species will only persist in iron-limited environments. The formation and fate of thioarsenic species in the environment are not fully understood. New experimental data are needed to explore arsenic sulfide solubility in the context of the multiple thioarsenic species documented here. Because natural aquatic systems are often highly undersaturated with respect to pure arsenic sulfide phases, adsorption and co-precipitation processes involving thioarsenites require investigation.

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