



# Reassessing the role of sulfur geochemistry on arsenic speciation in reducing environments

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## ABSTRACT

Recent evidence suggests that the oxidation of arsenite by zero-valent sulfur (S(0)) may produce stable aqueous arsenate species under highly reducing conditions. The speciation of arsenic (As) in reducing soils, sediments and aquifers may therefore be far more complex than previously thought. We illustrate this by presenting updated  $E_h$ -pH diagrams of As speciation in sulfidic waters that include the most recently reported formation constants for sulfide complexes of As(III) and As(V). The results show that the stability fields of As(III) and As(V) (oxy)thioanions cover a large pH range, from pH 5 to 10. In particular, As(V)-S(-II) complexes significantly enhance the predicted solubility of As under reducing conditions. Equilibrium calculations further show that, under conditions representative of sulfidic pore waters and in the presence of solid-phase elemental sulfur, the  $S^0_{(aq)}/HS^-$  couple yields a redox potential ( $E_h$ )  $\sim 0.1$  V higher than the  $SO_4^{2-}/HS^-$  couple. S(0) may thus help stabilize aqueous As(V) not only by providing an electron acceptor for As(III) but also by contributing to a more oxidizing redox state.

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## 1. Introduction

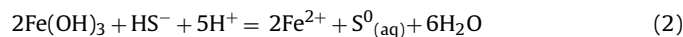
The biogeochemical cycling of sulfur (S) influences the environmental fate and transport of arsenic (As) and other elements. Sulfur transformations, in particular the microbially mediated reduction of sulfate ( $SO_4^{2-}$ ), are closely related to redox conditions, which, in turn, control the speciation of metalloids [1]. Sulfide can also form complexes with these elements and, hence, may significantly enhance their mobility in anoxic environments. Aqueous sulfide complexes may even persist in oxygenated water bodies due to their kinetic stability [2]. Metalloids may further precipitate as discrete sulfide minerals or sorb to iron (Fe) sulfide phases such as mackinawite ( $FeS_{m(s)}$ ) and pyrite ( $FeS_{2(s)}$ ) [3–5]. Microbial sulfate reduction is thus expected to play a leading role in determining whether or not trace elements such as As accumulate to toxic levels in natural waters.

Two key redox-active products of microbial  $SO_4^{2-}$  reduction in reducing environments are dissolved sulfide and zero-valent sulfur ( $S^0_{(aq)}$ ). Free sulfides, which exist primarily as  $H_2S$  and  $HS^-$  at circumneutral pH ( $pK_a = 7.02$ ), are powerful reductants (Fig. 1). In many natural waters, the build-up of aqueous  $Fe^{2+}$  is limited by its reaction with  $H_2S$  and  $HS^-$  through the precipitation of  $FeS_{m(s)}$  [6]:



Although in most low-temperature geochemical environments Fe monosulfides are less stable than pyrite, they are the first to form [5] and therefore  $FeS_{m(s)}$ , rather than  $FeS_{2(s)}$ , tends to control the solution chemistry in these environments. In sulfate reducing conditions that contain ferric iron (Fe(III)) mineral phases, the rapid reaction between  $HS^-$  and Fe(III) produces ferrous iron (Fe(II)), which then precipitates as additional  $FeS_{m(s)}$ , provided that  $HS^-$  is present in excess. This reaction sequence is one of the key pathways for  $S^0_{(aq)}$  production.

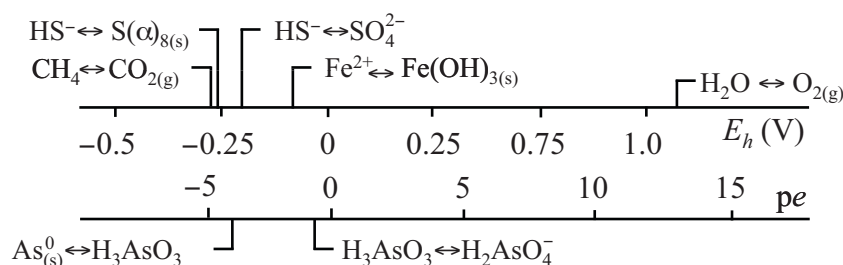
The generation of  $S^0_{(aq)}$  through the abiotic reaction of dissolved sulfide with Fe(III) (hydr)oxides can be represented by [7]:



The corresponding reaction mechanism is summarized as follows by Kocar and Fendorf [8]. The ligand displacement of  $OH^-$  by  $HS^-$  and subsequent electron transfer from S(-II) to Fe(III) forms a  $Fe^{II}-S^\bullet$  complex, whose dissociation then produces  $Fe^{2+}$  and  $S^0_{(aq)}$ . Inorganic polysulfides ( $S_{n+1}^{2-}$  and their protonated forms), which are unbranched chain polymers comprised of  $n$  atoms of S(0) and one S(-II), are then readily formed in the presence of  $HS^-$  [9,10], hence consuming some of the  $S^0_{(aq)}$ .

It has long been recognized that  $S^0_{(aq)}$  may influence the redox potential ( $E_h$ ) in sulfidic environments. At fixed pH, increasing the  $S^0_{(aq)}/HS^-$  ratio raises the potential measured by a platinum electrode (e.g., [11]). Moreover, solutions containing both  $S^0_{(aq)}$  and  $HS^-$  can affect the redox state of anion-forming metalloids through complex formation [12–14]. Thus, under conditions where microbial  $SO_4^{2-}$  reduction occurs in the presence of reactive Fe(III)

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**Fig. 1.** Redox scales showing the equilibrium redox potentials ( $E_h$  in V) and corresponding  $pe$  values for a number of environmentally relevant redox couples at  $pH = 7$ . Note that the activities of all species are set to unity (standard state), except for  $Fe^{2+}$  and  $\Sigma CO_3^{2-}$ , for which concentrations of  $1 \times 10^{-5}$  M and  $3 \times 10^{-3}$  M are assigned, respectively.

mineral phases, and where the build-up of dissolved  $Fe^{2+}$  is prevented by the precipitation of Fe sulfides (Eq. (1)), two sulfur redox couples can potentially influence the redox potential of the aqueous phase:  $SO_4^{2-}/HS^-$  and  $S^0_{(aq)}/HS^-$  (Fig. 1). Yet, in most of the existing geochemical models of sulfidic waters, only the redox couple  $SO_4^{2-}/HS^-$  is used to estimate the redox potential and compute the speciation of redox-sensitive elements. This implicitly assumes that this couple is at equilibrium and that the  $S^0_{(aq)}/HS^-$  couple exerts no control on redox conditions and redox speciation. In many cases, this may be poor assumptions.

In this contribution, we determine the potential influence of  $S^0_{(aq)}$  on the  $E_h$  of sulfidic waters using equilibrium thermodynamic calculations. We further assess how the inclusion or not of  $S^0_{(aq)}$  in these calculations affects the theoretical speciation of As, a toxic, redox-sensitive metalloid of global concern (e.g., [15]). We also compare the  $E_h$ - $pH$  stability diagrams (Pourbaix, or predominance diagrams) of As predicted based on the two thermodynamic databases for (oxy)thioarsenic species presented by Wilkin et al. [16] and Helz and Tossell [13], respectively.

## 2. Modeling approach

### 2.1. Equilibrium calculations

Because of practical difficulties associated with the experimental characterization of the speciation of trace elements in sulfidic environments (e.g., [17,18]), geochemical equilibrium models remain very popular. These models are powerful tools to help design remediation strategies, predict the evolution of water quality and focus experimental studies [19]. Even though thermodynamic equilibrium is often not attained in natural waters, equilibrium-based models can be used to define the endpoint and direction of geochemical processes. The crucial step when building a speciation model is the selection of the chemical species to be included and their thermodynamic properties. Particular attention should be given to the internal consistency of the thermodynamic database. For the case of As, thermodynamic constants have been critically reviewed by Nordstrom and Archer [20] and, more recently, by Lu and Zhu [21]. It should be noted, however, that the latter authors overlooked the most recent thermodynamic data for As speciation in sulfidic waters [13,16].

The  $E_h$  and  $pH$  are compulsory inputs to geochemical speciation models of redox-sensitive elements. While  $pH$  measurements are straightforward, measuring the redox potential directly in natural solutions is far more problematic [19,22]. Alternatively, the concentrations of dominant redox active species, for instance  $O_2$ ,  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $SO_4^{2-}$ ,  $S^0_{(aq)}$ , and  $HS^-$ , can be measured and the equilibrium  $E_h$  can be calculated based on the Nernst equation:

$$E_h = E^0 + \frac{RT}{\nu F} \ln \frac{a_{ox}}{a_{red}} \quad (3)$$

where  $E^0$  is the standard redox potential, relative to the standard hydrogen electrode, of the redox couple under consideration,  $a_{ox}$  and  $a_{red}$  are the activity product of the oxidized and reduced species, respectively,  $R$  is the ideal gas constant ( $8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  denotes the absolute temperature (K),  $\nu$  is the number of transferred electrons ( $e^-$ ), and  $F$  is Faraday's constant ( $96,484 \text{ J V}^{-1} \text{ mol}(e^-)^{-1}$ ). To calculate the equilibrium composition of a chemical system,  $E_h$  can be converted to a  $pe$  value, that is the negative logarithm of the hypothetical electron activity in the aqueous solution, using:

$$pe = \frac{E_h F}{2.303 RT} \quad (4)$$

### 2.2. Zero-valent sulfur

In order to use the  $S^0_{(aq)}/HS^-$  redox couple in  $E_h$  calculations, the concentration of  $S^0_{(aq)}$  must first be estimated. Total aqueous concentrations of zero-valent sulfur,  $\Sigma S(0)$ , and total divalent sulfur,  $\Sigma S(-II)$ , are typically the measured observables in experiments and field samples. They are defined as follows:

$$\Sigma S(0) = [S^0_{(aq)}] + \sum n [H_x S_n S^{x-2}] \quad (5)$$

and

$$\Sigma S(-II) = [H_2S] + [HS^-] + \sum [H_x S_n S^{x-2}] \quad (6)$$

where  $n$ , the number of zero-valent S atoms in a given polysulfide species, varies between 1 and 7, and  $x$ , the number of H atoms, varies between 0 and 2. The concentrations of individual polysulfide species are calculated from the mass balances (Eqs. (5) and (6)) and the mass action law equations for the formation of the polysulfide species. Reactions for the formation of the polysulfide species can be implemented in existing speciation computer programs to calculate the speciation of zero-valent S, provided that  $S^0_{(aq)}$  is added as a component. The concentrations of polysulfides and aqueous  $S^0_{(aq)}$  can then be computed based on measured values of  $\Sigma S(0)$ ,  $\Sigma S(-II)$  and  $pH$ , using the appropriate thermodynamic constants [9].

While methods to measure nano-molar levels of  $\Sigma S(0)$  have been available for several years [10,23–26], the scarcity of  $\Sigma S(0)$  data partly reflects interferences due to oxidation artifacts during sampling and analysis [24]. In the absence of  $\Sigma S(0)$  measurements, its equilibrium with respect to rhombic crystalline elemental sulfur ( $S(\alpha)_{8(s)}$ ) can be assumed [24]:

$$\frac{1}{8} S(\alpha)_{8(s)} = S^0_{(aq)} \quad \log K = -6.68 \quad (7)$$

This is a reasonable assumption, as  $S^0_{(aq)}$  and polysulfides have been shown to closely approach equilibrium with  $S(\alpha)_{8(s)}$  for a variety of microbial [27] and geochemical processes under anoxic conditions [24]. In particular, Wang and Tessier [24] report that the anoxic porewaters of lake sediments are close to saturation, or slightly super-saturated, with respect to  $S(\alpha)_{8(s)}$ .

### 2.3. Software and thermodynamic databases

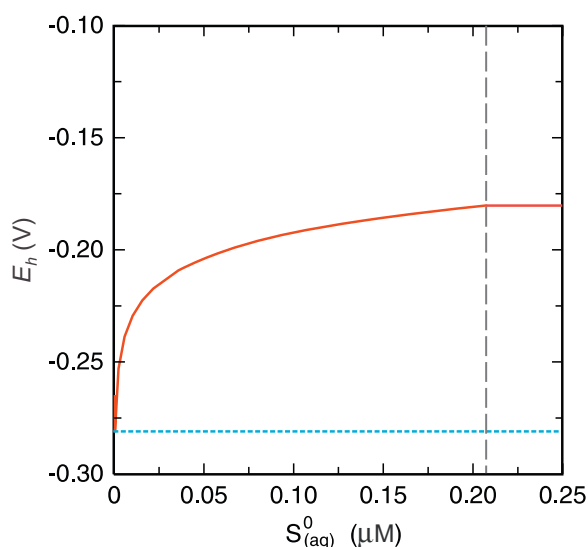
Equilibrium  $E_h$ ,  $pe$  values and As speciation presented here were calculated at 298.15 K and 1 bar with the public domain computer code PHREEQC Version 2.17.5 [28]. The thermodynamic database WATEQ4F imbedded within PHREEQC was updated by including equilibrium constants for (i) the ionization of As(III) and As(V) oxyacids [20], (ii) the sulfidation of As(III) species [16] or the sulfidation of As(III) and As(V) species [13], (iii) elemental sulfur solubility (Eq. (7) and Ref. [24]), (iv) the formation of polysulfide species [9], and (v) As mineral solubilities [20]. A table of these equilibrium constants is given in Appendix (Table A1). Note that the constants for the (oxy)thioarsenic species differ between the thermodynamic databases of Wilkin et al. [16] and Helz and Tossell [13]. The  $E_h$ -pH diagrams were generated using the beta version of the public domain computer code PhreePlot [29].

## 3. Results and discussion

### 3.1. Elemental sulfur and the $E_h$ of sulfidic waters

A sulfidic solution containing  $1 \times 10^{-4}$  M of  $\Sigma S(-II)$  and  $1 \times 10^{-9}$  M of  $\Sigma S(VI)$  has a theoretical  $E_h$  of  $-0.28$  V ( $pe = -4.7$ ) if the redox state is controlled by the  $SO_4^{2-}/HS^-$  couple ( $pH = 7$ ). In contrast, when elemental sulfur is present in the system and  $S^0_{(aq)}/HS^-$  is the dominant redox couple, more oxidizing  $E_h$  values are predicted under otherwise identical conditions (Fig. 2). The  $E_h$  increases with increasing  $S^0_{(aq)}$  concentration, until the solution reaches equilibrium with  $S(\alpha)_{8(s)}$ , beyond which, in principle,  $S^0_{(aq)}$  no longer accumulates in the aqueous phase. The theoretical  $E_h$  of such a sulfidic solution at equilibrium with  $S(\alpha)_{8(s)}$  is  $-0.18$  V ( $pe = -3.0$ ), which is  $0.10$  V ( $1.7$   $pe$  units) higher than that predicted using the  $SO_4^{2-}/HS^-$  couple.

The  $S^0_{(aq)}/HS^-$  couple is expected to contribute to the redox potential in sulfidic environments where elemental sulfur is actively forming [11,24,25,27,30]. For these environments, the  $E_h$  at equilibrium with  $S(\alpha)_{8(s)}$  represents a relevant theoretical end-member. The results in Fig. 2 imply that the  $S^0_{(aq)}/HS^-$  redox couple yields more oxidizing conditions than the  $SO_4^{2-}/HS^-$  couple, which



**Fig. 2.** Predicted equilibrium redox potential ( $E_h$ ) for the  $S^0_{(aq)}/HS^-$  redox couple (solid line) in sulfidic waters at  $pH = 7$  ( $\Sigma S(-II) = 1 \times 10^{-4}$  M and  $\Sigma S(VI) = 1 \times 10^{-9}$  M) as a function of the dissolved elemental sulfur concentration. For comparison, the dotted line corresponds to the  $E_h$  calculated for the  $SO_4^{2-}/HS^-$  redox couple. The vertical dashed line indicates the  $S^0_{(aq)}$  concentration at which saturation with respect to  $S(\alpha)_{8(s)}$  is reached.

is opposite to what is expected when standard states are assumed for the sulfur species, as in Fig. 1. Values of  $E_h$  at standard state frequently displayed on redox scales are therefore not realistic for natural sulfidic waters, which typically have  $SO_4^{2-}/HS^-$  concentration ratios that deviate significantly from one. Similar departures from  $E_h$  at standard state are also expected with changes in temperature and/or pressure (e.g., [31]).

### 3.2. As speciation in sulfidic environments

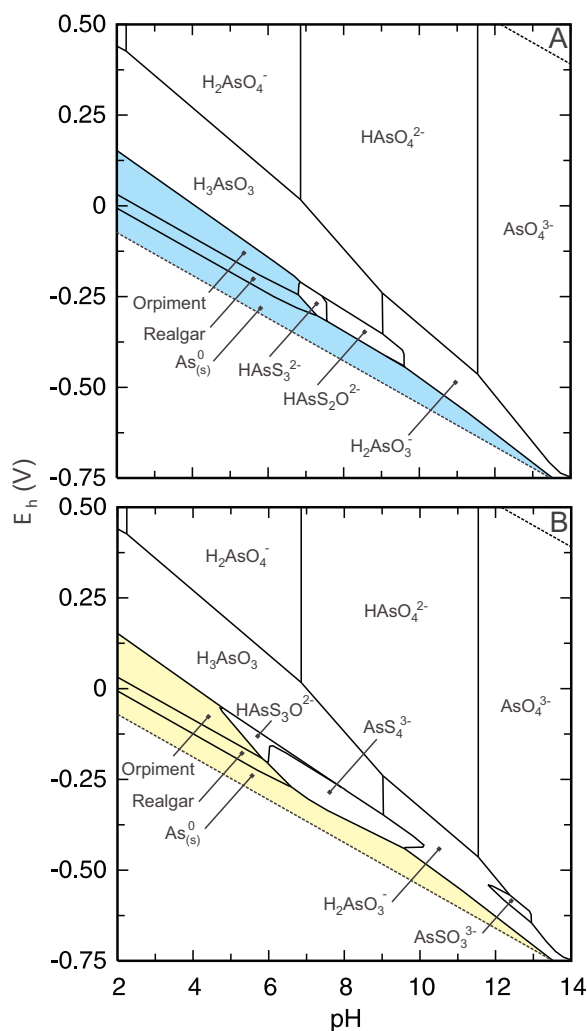
To our knowledge, the latest critical review of thermodynamic data for As is that of Lu and Zhu [21]. In presenting As speciation in sulfidic waters, these author selected the thermodynamic data presented by Webster [32]. Since the work by Webster [32], however, the formation constants of thioarsenic species have been revised in depth on two occasions, namely by Wilkin et al. [16] and Helz and Tossell [13].

Wilkin et al. [16] estimated the thermodynamic properties of As(III) thioanions. Their data have been used in a number of subsequent studies to calculate As speciation in sulfidic waters, assuming that only the reduced +III oxidation state is stable in these environments. Most studies further assume that the  $SO_4^{2-}/HS^-$  is the potential-determining redox couple in anoxic aquatic environments [33–39]. However, the analytical results of Wilkin et al. [16] as well as their assumption that only As(III) is stable in sulfidic waters have been challenged by laboratory experiments [17,40–43] and ab-initio calculations [13]. The accumulating evidence indicates that a range of dissolved As(V) species (thio and oxythioarsenates) may form, likely through As(III) oxidation by  $S^0_{(aq)}$ , and that these species may dominate aqueous As speciation due to their high stability. It has also been proposed that As(V) species may be an important sink for As in reducing lake sediments [44]. However, there have been few attempts to directly measure (oxy)thioarsenates species in the environment so far [41,43,45] and environmental fate models have yet to account for these species.

Helz and Tossell [13] have proposed a preliminary thermodynamic model which predicts the concentrations of 32 As(III) and As(V) (oxy)thio-monomers as a function  $pH$ ,  $\Sigma S(-II)$  and  $\Sigma As_{(aq)}$  at any imposed  $E_h$ . Their model reproduces the previously measured solubility of the mineral orpiment ( $As_2S_3$ ) and predicts a significant contribution of As(V) species under highly reducing conditions. The most important implication of the new model is that it allows for the existence of both As(III) and As(V) thioanions under highly reducing conditions.

Wilkin et al. [16] and Helz and Tossell [13] models are built on different assumptions and, as such, the two thermodynamic databases should not be mixed together, as has been done (e.g., [46]). The differences between the predictions of the two models are illustrated in Fig. 3, where the  $E_h$ - $pH$  diagram in Fig. 3A only accounts for the formation of thioarsenites using the equilibrium constants provided in [16], while the  $E_h$ - $pH$  diagram in Fig. 3B allows for both thioarsenites and thioarsenates formation according to [13] (see Table A1 for a list of the thermodynamic constants). Because both Wilkin et al. [16] and Helz and Tossell [13] consider the same equilibrium constants for the ionization of As(III) and As(V) oxyacids [20], the upper parts of the  $E_h$ - $pH$  diagrams in Fig. 3 are identical. In the lower portions of the diagrams, however, the predicted As speciation differs significantly between the two models.

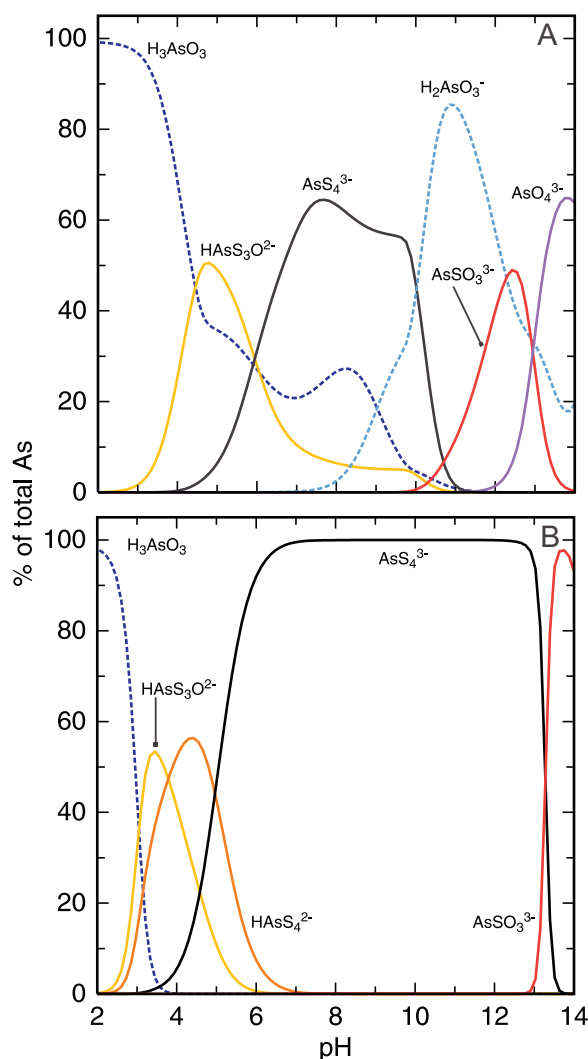
According to the  $E_h$ - $pH$  diagram based on the Wilkin et al. [16] model (Fig. 3A), two aqueous thioarsenite species occupy narrow stability fields under reducing conditions:  $HAs(III)S_3^{2-}$  and  $HAs(III)S_2O_2^-$ , which dominate at  $pH > 6.25$  and  $pH > 7.25$ , respectively. In contrast, the Helz and Tossell [13] model predicts that the thioarsenate species  $HAs(V)S_3O_2^-$  dominates at  $pH < 6$  and tetrathioarsenate ( $As(V)S_4^{3-}$ ) dominates at higher  $pH$ . The notable prevalence of the deprotonated  $As(V)S_4^{3-}$  at  $pH > 6$



**Fig. 3.**  $E_h$ -pH diagrams for the As-O-H-S system ( $\Sigma S = 1 \times 10^{-4}$  M and  $\Sigma As = 2 \times 10^{-5}$  M). The diagrams in panels A and B are based on the (oxy)thioarsenic species and corresponding thermodynamic data provided in Refs. [16,13], respectively. Equilibrium with  $S(\alpha)_{8(s)}$  is imposed for the diagram in panel B. The shaded areas indicate the predominance of solid As phases. The equilibrium constants used to construct the diagrams are given in Table A1.

reflects the tendency of thioanions to be stronger acids than oxyanions [13]. Monothioarsenate ( $As(V)SO_3^{3-}$ ) has a small stability field at very high pH. Both diagrams shown in Fig. 3 imply that the inclusion of (oxy)thioarsenic species reduces the stability fields of the orpiment ( $As_2S_3$ ) and realgar ( $AsS$ ) mineral phases appreciably, which suggest that these minerals are less likely to form than expected from previously published  $E_h$ -pH diagrams for the As-O-H-S system using similar  $\Sigma S(-II)$  concentrations [20,21,36,47,48].

The interconversion of As(III) and As(V) species in highly reducing environments requires the presence of appropriate electron donors and acceptors. In these environments, the  $SO_4^{2-}$  concentration is typically vanishingly small. For instance, at pH=7,  $\Sigma S = 1 \times 10^{-5}$  M and  $E_h = -0.25$  V, the theoretical  $SO_4^{2-}$  concentration is  $1.5 \times 10^{-10}$  M. Thus, while in principle the  $SO_4^{2-}/HS^-$  couple can be used to compute a redox potential,  $SO_4^{2-}$  is a virtual electron acceptor. As discussed in Section 3.1, a more likely electron acceptor in sulfidic environments is  $S^0_{(aq)}$ . Experimental data further suggest that  $S^0_{(aq)}$  oxidizes As(III) to As(V). The important effect that  $S^0_{(aq)}$  and polysulfides may exert on As speciation is shown in Fig. 4, where we compare the aqueous equilibrium speciation of As as a function of pH when  $S(\alpha)_{8(s)}$  is either absent (Fig. 4A) or present



**Fig. 4.** Predicted relative abundances of dissolved As(V) (solid lines) and As(III) species (dashed lines) as a function of pH using the equilibrium constants for (oxy)thioarsenic species from Helz and Tossel [13] ( $\Sigma S(-II) = 1 \times 10^{-4}$  M and  $\Sigma As = 2 \times 10^{-5}$  M). In panel A,  $E_h$  is assumed to be controlled by the redox couple  $SO_4^{2-}/HS^-$  and in panel B by the redox couple  $S^0_{(aq)}/HS^-$ .

in excess (Fig. 4B). When  $S^0_{(aq)}$  is omitted (Fig. 4A), the  $SO_4/HS^-$  couple controls the  $E_h$  and thus As(V) thioanions dominate the predicted As speciation within the pH range pH 5–10, outside which the arsenite species  $H_3As(III)O_3^0$  and  $H_2As(III)O_3^-$  prevail. In contrast, when including  $S^0_{(aq)}$  in the model calculations (Fig. 4B), As(V) (oxy)thioanions dominate the predicted As speciation from pH 3.5 and up. With increasing pH,  $HA(SV)S_3O_2^-$  is formed first, followed by  $HA(SV)S_4^{2-}$ ,  $As(V)S_4^{3-}$  and  $As(V)SO_3^{3-}$ .

Under sulfidic conditions similar to those imposed in the above modeling exercise (Fig. 4B), we hypothesize that (oxy)thioarsenates form through the oxidation of (thio)arsenite by  $S^0_{(aq)}$ , in a manner similar to the procedure used to prepare thioarsenate salts in the laboratory (e.g., [41]). Another possible formation mechanism is the dissolution of naturally occurring minerals, such as copper (Cu) tetrathioarsenic (enargite;  $CuAsS_4(s)$ ), which is thought to yield aqueous  $As(V)S_4^{3-}$  [49,50]. It is worth mentioning that the prevalence of aqueous As(V) species has also been documented for reducing Fe(II)-rich waters [51]. Under such conditions, aqueous Fe(II) and  $As(V)O_4^{3-}$  have been shown to precipitate as symplectite ( $Fe_3(AsO_4)_2 \cdot 8H_2O(s)$ ) rather than undergoing electron transfer [52].



#### 4. Conclusions

Arsenic contamination of water resources is a major environmental and health concern in many parts of the world. Arsenic mobility is strongly linked to the redox environment, with reducing conditions typically causing the release of As to solution, hence increasing its bioavailability and toxicity. Here we show, using thermodynamic calculations, that the speciation of As under reducing conditions may be closely linked to that of sulfur. The theoretical results provide a quantitative and testable framework that can help guide future experimental studies of As speciation in sulfidic waters.

The following conclusions can be drawn from the equilibrium speciation results presented.

1. Zero-valent sulfur may play a major role in sulfidic environments through its effect on the redox potential and as an electron acceptor for the oxidation of As(III). We strongly recommend more systematic measurements of dissolved  $S^0_{(aq)}$  concentrations, particularly in environments where microbial  $SO_4^{2-}$  reduction takes place in the presence of Fe(III) minerals.
2. In the presence of free sulfide, the modeling results suggest that the oxidation of As(III) by zero-valent sulfur can produce As(V) (oxy)thioanions. These species are thermodynamically stable over a large pH range thereby reducing the stability fields of arsenite mineral phases. The formation of arsenate–sulfide complexes is thus one mechanism that helps explain the increased solubility and mobility of As in reducing environments.
3. The  $S^0_{(aq)}/HS^-$  redox couple may have similar effects on the speciation and mobility of other redox-sensitive anion-forming metalloids, in particular Sb [14] and Se. The effects, however, are expected to be less pronounced than for As, because the Sb(V)/Sb(III) and Se(VI)/Se(IV) redox transitions occur at more oxidizing redox potentials than the As(V)/As(III) transition.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.02.029.

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