Quantitative determination of elemental sulfur at the arsenopyrite surface after oxidation by ferric iron: mechanistic implications

Molly M. McGuire,[a] Jillian F. Banfield[b] and Robert J. Hamers*[a]

[a]Department of Chemistry, 1101 University Ave, University of Wisconsin—Madison, Madison, WI 53706, USA. E-mail: rjhamers@facstaff.wisc.edu; Tel: (608) 262-6371; Fax: (608) 262-0453
[b]Department of Geology and Geophysics, 1215 W. Dayton St, University of Wisconsin— Madison, Madison, WI 53706, USA

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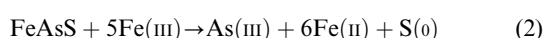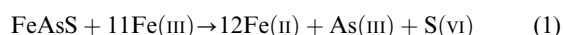
The elemental sulfur formed at the arsenopyrite surface after oxidation by ferric iron was quantitatively measured by extraction in perchloroethylene and subsequent quantitative analysis by HPLC. Reactions with ferric iron in perchloric acid solutions or in sulfuric acid solutions (both at pH = 1 and 42 °C, which approximate extreme acid mine drainage conditions) produced elemental sulfur in quantities greater than 50% of the total reacted sulfur. The controversy surrounding the mechanism of the oxidative dissolution of arsenopyrite is discussed in light of these measurements. Based on the observation of greater than 50% production of elemental sulfur, a mechanism by which all the sulfur from the mineral proceeds through thiosulfate can be eliminated as a possible description of the dissolution of arsenopyrite. Instead, it is likely the other constituents of the mineral lattice, Fe and As, are leached out, leaving behind a S^0 lattice. Nucleation reactions will then result in the formation of stable S_8 rings.

Introduction

Arsenopyrite, FeAsS (a derivative of the marcasite structure), is the most common arsenic-bearing mineral. Under oxidizing conditions, either occurring naturally or as a result of mining processes, the mineral produces arsenite (AsO_3^{3-}), arsenate (AsO_4^{3-}), and sulfate (SO_4^{2-}),[1–3] thus contributing to the acidification of water as well as the release of soluble arsenic species. Despite the potential environmental and health hazards posed by the oxidative dissolution of arsenopyrite, the mineral has received far less attention in the laboratory than pyrite (FeS_2), the most studied of the sulfide minerals.

In acidic environments, the rate of sulfide mineral dissolution is typically limited by the supply of ferric iron, Fe^{3+}; however, in the presence of iron-oxidizing microorganisms, the supply of ferric iron is continuously replenished by microbial oxidation of the ferrous iron released from sulfide minerals.[4] Despite the importance of oxidation by ferric iron in natural systems, many of the fundamental details of the oxidation of arsenopyrite by Fe^{3+} under acidic conditions still remain unclear. One critical issue is the stoichiometry of the reaction with respect to the sulfur species. The literature is divided about whether the majority of the sulfur from the mineral is released into solution as sulfoxy anions[5,6] [in a scheme similar to eqn. (1)], or whether a substantial amount of the sulfur remains as insoluble elemental sulfur (S_8) at the mineral surface[7,8] [as shown in eqn. (2)]:

$$FeAsS + 11Fe(III) \rightarrow 12Fe(II) + As(III) + S(VI) \quad (1)$$

$$FeAsS + 5Fe(III) \rightarrow As(III) + 6Fe(II) + S(0) \quad (2)$$

Previous efforts to characterize the arsenopyrite surface by scanning electron microscopy (SEM) after leaching reactions with ferric iron found no evidence of elemental sulfur on the mineral surface.[5,7] Other studies, using X-ray photoelectron spectroscopy (XPS), did not detect elemental sulfur on arsenopyrite surfaces that were exposed to mine wastewaters.[1]

In contrast, Raman spectroscopic and chromatographic investigations of arsenopyrite samples oxidized in ferric iron solutions identified elemental sulfur as the major reaction product.[9] Additionally, numerous studies of the oxidation of arsenopyrite in the presence of iron-oxidizing microorganisms have revealed the presence of significant quantities of elemental sulfur at the mineral surface.[10–14] Clearly, the distribution and abundance of sulfur oxidation products is still a matter of much debate.

One possible explanation for the diversity of findings regarding elemental sulfur on arsenopyrite is the chemical modification of the mineral surface during analysis. Both SEM and XPS are vacuum-based techniques which employ electrons and X-rays, respectively, capable of volatilizing high vapor pressure surface products such as elemental sulfur.[15] Raman spectroscopy, which uses lower-energy excitation in the visible region of the spectrum and can be performed at ambient pressures, is well suited to investigations of elemental sulfur on sulfide mineral surfaces.[16] The difficulties, however, of producing a calibration standard with a uniform dispersion of elemental sulfur on the mineral surface limit the application of this method to semi-quantitative studies.[14]

A quantitative determination of the distribution of sulfur reaction products is necessary for mechanistic investigations. Fernandez, et al.[17] measured elemental sulfur on electrochemically oxidized arsenopyrite samples by extracting the elemental sulfur in carbon disulfide and weighing the evaporative residues. Although the extraction method allowed them to quantitatively collect the elemental sulfur from the mineral surface, the lack of selectivity and the low sensitivity of the mass measurement severely limited the accuracy of the elemental sulfur determination.

The recent development of a new technique in our laboratory, involving the extraction of the elemental sulfur from the mineral surface with an organic solvent and subsequent analysis by HPLC, allowed us to make the first quantitative measurements of the abundance of elemental sulfur on sulfide mineral surfaces after reaction under oxidative

conditions.[9] We report here the determination of elemental sulfur at the arsenopyrite surface after reaction with acidic, ferric iron solutions. These quantitative measurements place restrictions on any proposed mechanism of arsenopyrite oxidation and rule out the possibility that elemental sulfur is solely a product of thiosulfate decomposition in acid.

Experimental

The oxidation of arsenopyrite by ferric iron in acidic solutions was investigated. All reactions were performed at pH = 1 and 42 °C. These temperature and pH conditions were chosen in order to simulate extreme AMD conditions[18] in the laboratory. Although sulfuric acid solutions provide a closer approximation to actual environmental conditions, perchloric acid solutions were also studied because they allow for the determination of total aqueous sulfur without the difficulties of a large sulfate background.

Mineral preparation

Arsenopyrite of Portuguese origin (Ward's Natural Science) was crushed by hand using a mortar and pestle and then sieved. The 75–150 μm fraction was retained and repeatedly rinsed with ethanol. Ultrasonic treatment in ethanol for 30 min freed any adhering smaller particles and organic compounds. To remove any oxide layer that may have formed on the arsenopyrite surface in air, the mineral samples were treated with a 50% solution of HCl for several hours. Previous studies have demonstrated that acid-cleaned sulfide mineral surfaces exhibit similar reactivity to a freshly cleaved surface.[19] Finally, the mineral was placed in 10 mL of carbon disulfide for several hours and then rinsed twice with an additional 5 mL. We have shown previously that this pretreatment step effectively removes any elemental sulfur already present on the mineral surface and produces clean starting material for subsequent investigations.[9]

Oxidation experiments

Ferric iron solutions were prepared by dissolving the appropriate amount of ferric perchlorate (GFS Chemicals, reagent grade) or ferric sulfate (Alfa AESAR, reagent grade) in perchloric or sulfuric acid solutions (pH = 1), respectively. A control experiment in perchloric acid without ferric iron revealed that the extent of oxidation that can be attributed to the perchlorate ion itself is negligible. This finding is in agreement with a previous study, which showed that the perchlorate ion has no effect on the rate of dissolution of pyrite.[20]

The conditions of the reaction, the duration of the oxidation experiment, and the amount of arsenopyrite material in each of the experiments are summarized in Table 1. Each reaction solution was initially purged for several hours with nitrogen (99.998%) in order to saturate the solution and remove most of the oxygen prior to the start of the experiment. The nitrogen was run through a sparging flask consisting of a fritted glass aerator submerged in a flask of distilled water. The top of the sparging flask was fitted with a Teflon cap that held several pieces of 0.010″ inner diameter Tefzel tubing. Each length of the small diameter tubing ran to a separate 125 mL Erlenmeyer flask containing 100 mL of the appropriate reaction solution. The tubing was passed through a septum on the top of the flask and submerged in the acidic solution. A short length of slightly larger diameter tubing was also fit into the septum and served as the gas outlet on each reaction flask.

To begin the oxidation experiment, the mineral sample was added to the flask, and the septum was quickly replaced. After addition of the mineral, the gas flow was maintained at a suitable rate to sustain saturation. All reaction and sparging flasks were kept at 42.0 ± 0.1 °C for the duration of the experiment in a constant-temperature incubator (Fisher Scientific).

Elemental sulfur extraction and analysis

The method we developed for quantification of elemental sulfur by extraction with perchloroethylene, and subsequent analysis by high-performance liquid chromatography is described elsewhere in detail.[9] In summary, Raman spectroscopic investigations of oxidized arsenopyrite surfaces before and after extraction in perchloroethylene confirmed that elemental sulfur formed on the mineral surface during oxidation is not present after the extraction process. Additionally, Raman spectroscopic analyses of the evaporative residues of the perchloroethylene solution confirmed that elemental sulfur was present in the extract solution.

Most of the acidic reaction solution was carefully decanted from the reaction flask, leaving as much of the solution as necessary to avoid losing any mineral material. 25 mL of perchloroethylene (Acros, spectrophotometric grade) was added to the reaction flask that contained the mineral sample and the remaining aqueous reaction solution. The denser perchloroethylene, which displaces the aqueous phase at the bottom of the unstirred flask, was left in contact with the mineral overnight (8–16 h) at room temperature. After completion of the extraction, the liquid contents of the reaction flask were poured into a separatory funnel, and an aliquot of the bottom perchloroethylene layer was drawn off for analysis by HPLC.

HPLC analyses were performed on either a Shimadzu LC-10AT high-performance liquid chromatography system with an SPD-M10AV diode array detector, or a Shimadzu SCL-10A. On both systems, an Alltech Econosphere 5 μ C_{18} reverse-phase column (4.6 × 250 mm) was used with an eluent comprised of 95% methanol (Fisher, electronic grade): 5% water mixture at a flow rate of 1 mL min^{-1}. The injection volume for all analyses was 20 μL. Absorption at 254 nm was used for detection, and data were collected on a PC running the Shimadzu Class-VP Chromatography Data System. The areas of the elemental sulfur peak for a series of standards were used to determine the concentration of elemental sulfur extracted in each sample. Linear regression analysis of the calibration points yielded an r^2 value of at least 0.9998 for all analyses. Because of the exceptional goodness of fit of the calibration

Table 1 Experimental parameters

Sample number	Acid and total volume	Oxidant	Mineral material/g	Length of reaction/d
PC1	Perchloric, 75 mL	310 ppm Fe^{3+}	0.324	4
PC2	Perchloric, 75 mL	310 ppm Fe^{3+}	0.326	4
PC3	Perchloric, 75 mL	310 ppm Fe^{3+}	0.328	4
PC4	Perchloric, 75 mL	310 ppm Fe^{3+}	0.348	4
PC5	Perchloric, 75 mL	310 ppm Fe^{3+}	0.346	4
PC6	Perchloric, 75 mL	310 ppm Fe^{3+}	0.345	4
S1	Sulfuric, 100 mL	130 ppm Fe^{3+}	0.328	6
S2	Sulfuric, 100 mL	250 ppm Fe^{3+}	0.331	6
S3	Sulfuric, 100 mL	510 ppm Fe^{3+}	0.329	6

Table 2 Results of experiments in perchloric acid

Sample number	Elemental sulfur (HPLC)/μmoles	Total aqueous sulfur (ICP-AES)/μmoles	Total S-containing products/μmoles	Elemental sulfur: % total S-containing products	Aqueous As products/μmoles
PC1	28 ± 1	24 ± 1	52 ± 2	54 ± 3	56 ± 3
PC2	33 ± 2	20 ± 1	52 ± 2	62 ± 4	54 ± 3
PC3	33 ± 2	20 ± 1	53 ± 2	62 ± 4	51 ± 3
PC4	34 ± 2	19 ± 1	53 ± 2	64 ± 4	55 ± 3
PC5	30 ± 2	22 ± 1	53 ± 2	58 ± 4	58 ± 3
PC6	37 ± 2	21 ± 1	58 ± 2	64 ± 4	58 ± 3

data, the uncertainty in the measured concentrations can be approximated as the uncertainty in the weight measurement of the elemental sulfur used to produce the standards ($<5\%$).

Aqueous phase measurements

Total aqueous sulfur and arsenic were measured for the experiments in perchloric acid using inductively coupled plasma atomic emission spectrometry (ICP-AES). Analyses were performed on a Jarrell Ash IRIS high resolution ICP optical emission spectrometer. Uncertainties in all measurements were less than 5%.

For the experiments in sulfuric acid, total aqueous arsenic was measured by atomic absorbance spectrometry using a Solaar 969 spectrometer (Unicam) with an Arsenic Super Lamp (Photron). Triplicate measurements were averaged for the calibration standards as well as the samples. Linear regression analysis of the calibration data yielded an r^2 value of 0.9995. Uncertainties were estimated to be less than 5%.

Results

Table 2 presents the results of elemental sulfur analyses for the arsenopyrite samples oxidized in perchloric acid solutions. For each experiment, the table summarizes the number of moles of elemental sulfur extracted from the mineral surface, the total aqueous sulfur content, the total reacted sulfur (elemental sulfur extracted + total dissolved sulfur), the percentage of the total reacted sulfur that is found as elemental sulfur, and the total aqueous arsenic. In each case, the estimated experimental uncertainties in the HPLC and ICP measurements were used to calculate the uncertainty in the elemental sulfur percentage. Two particularly significant results are highlighted in Table 2. First, the total reacted sulfur is, within the experimental uncertainty, equal to the total aqueous arsenic; this implies that either total sulfur or total arsenic can be used as a measure of the extent of reaction. This relation is most easily seen in Fig. 1, which presents the total dissolved sulfur and total arsenic for each experiment. Secondly, the values in Table 2 indicate that elemental sulfur at the mineral surface accounts for 54–64% of the total reacted sulfur. These results are graphically illustrated
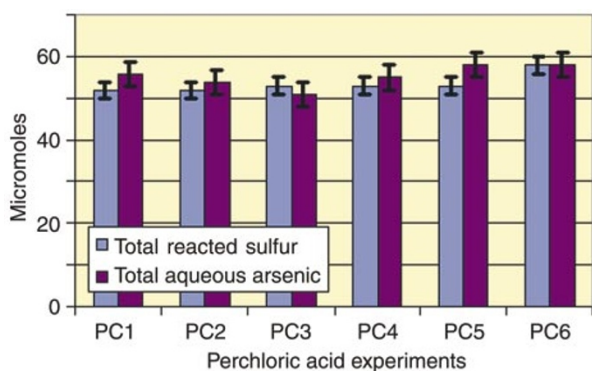
Fig. 2 Elemental sulfur as a percentage of the total of all sulfur-containing products (elemental sulfur + total aqueous sulfur) for each of the experiments in perchloric acid. Error bars represent uncertainties calculated from the experimental uncertainties in the individual measurements.

Table 3 Results of experiments in sulfuric acid

Sample number	Total aqueous As/μmoles	Elemental sulfur/μmoles	Elemental sulfur: % aqueous As
S1	30 ± 2	22 ± 1	74 ± 5
S2	54 ± 3	43 ± 2	81 ± 6
S3	97 ± 5	70 ± 3	72 ± 5

in Fig. 2. As will be discussed below, the fact that these numbers are significantly greater than 50% has important implications for the mechanism of arsenopyrite dissolution.

Table 3 presents the results of the three experiments conducted in sulfuric acid. Total moles of elemental sulfur and aqueous arsenic, as well as the measured elemental sulfur as a percentage of the total aqueous arsenic, are given. Experimental uncertainties from the measurements were propagated to calculate an uncertainty in the elemental sulfur percentage, which varied between 72 and 81%. These results are also summarized in Fig. 3. As one would expect, the different initial concentrations of oxidant produces significantly different extents of reaction, as evidenced by the increase in elemental sulfur and aqueous arsenic, as the concentration of ferric iron

Fig. 1 Total aqueous sulfur and total aqueous arsenic for each of the experiments performed in perchloric acid. All measurements were made with ICP-AES. Error bars indicate uncertainties in each measurement.
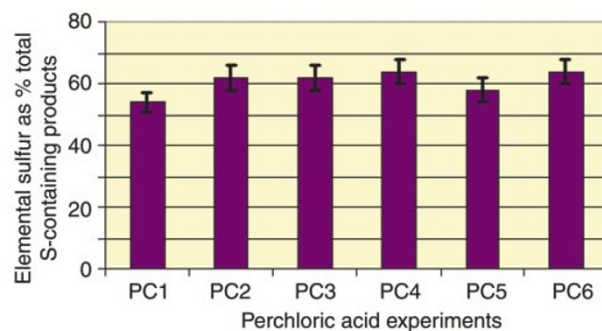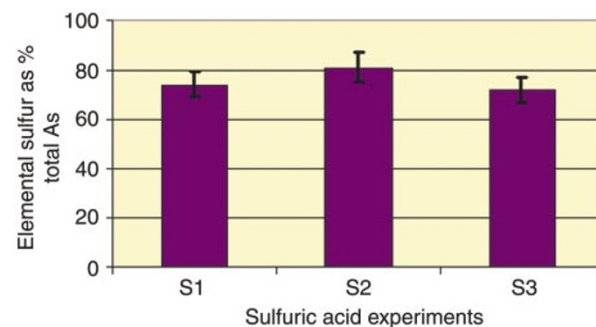
Fig. 3 Elemental sulfur as a percentage of the total aqueous arsenic for each of the experiments in sulfuric acid. Error bars represent uncertainties calculated from the experimental uncertainties in the individual measurements.

increased. However, in each case the percentage of elemental sulfur is approximately the same, representing between 72 and 81% of the total aqueous arsenic.

Discussion

Oxidation by ferric iron in perchloric acid

Based on the values shown in Table 2 and Fig. 2, it is clear that the percentage of elemental sulfur formed is greater that 50% of the total reacted sulfur for the arsenopyrite samples oxidized in perchloric acid solutions. The experimental uncertainties of 5% used to calculate the uncertainty in the final percentage are more than adequate to ensure that the actual concentrations fall within the given confidence intervals. Moreover, the two most likely causes of systematic error (elemental sulfur suspended in the aqueous phase, and changes in solution volume *via* evaporative loss) would both lead to an underestimate of the total sulfur present as elemental sulfur. Thus we believe that our observation—that greater than 50% of the total reacted sulfur is present as elemental sulfur—is well outside of any random or systematic errors.

Oxidation by ferric iron in sulfuric acid

The sulfuric acid system is perhaps a more interesting case because it is applicable to natural systems where the oxidation of sulfide minerals leads to sulfate production. From a practical standpoint, however, laboratory investigations of the sulfuric acid system are more difficult due to the large sulfate background signal that precludes the measurement of total aqueous sulfur released from the oxidized mineral. As a first approximation, the results of the perchloric acid experiments can be extrapolated to the case of oxidation by ferric iron in natural, sulfate-containing environments. Perchlorate and sulfate anions are both classified as 'hard' bases,[21] and thus are expected to form similar complexes and provide comparable chemical environments.

Another way to investigate the sulfuric acid system is to use a reaction variable other than total reacted sulfur to approximate the extent of reaction. For example, one could use total aqueous arsenic as a measure of the extent of reaction. The underlying assumption in this approach is that the total moles of arsenic in solution can be equated to the number of moles of arsenopyrite reacted. The aqueous concentration of arsenic is a valid measure of the extent of reaction only if there is no precipitation or other process that consumes oxidized species released from the bulk mineral. At the low pH conditions of this study, the high solubility of the probable oxygen-containing arsenic reaction products is expected to keep these products in solution. The solubility of arsenic in arsenic(III) oxide, As_2O_3, is slightly less than 0.2 M in 0.1 M H_2SO_4, whereas arsenic(v) oxide is even more soluble.[22] The arsenic levels measured in these experiments are all well below this concentration. Analysis of free energy data for the ferric arsenate–water system has shown that the solubility of arsenic is on the order of 0.05 M at pH 1.0.[23] Arsenic is also known to absorb strongly to iron hydroxides,[22] but based on the solubility product constants of iron hydroxides[24] (4.87×10^{-17} for ferrous hydroxide, 2.64×10^{-39} for ferric hydroxide), these species should also be very soluble at the extremely low pH conditions of this study.

The validity of equating total aqueous arsenic to total reacted sulfur is also confirmed in the data from the perchloric acid experiments. As can be seen in Table 2 and Fig. 1, the aqueous arsenic measurements for each experiment fall within several percent of the total reacted sulfur (elemental sulfur + aqueous sulfur). Thus, elemental sulfur as a percentage of total aqueous arsenic provides an equivalent measure of the percentage of sulfur-containing reaction products that is

found as elemental sulfur. In light of this relation, the data from the sulfuric acid experiments, as shown in Table 3, agree with our findings from the perchloric acid experiments. More than 50% of the total reacted sulfur is in the form of elemental sulfur.

Implications for the mechanism of oxidative dissolution

The fact that elemental sulfur accounts for more than half of the total sulfur has significant mechanistic implications. One possible reaction pathway for the oxidative dissolution of arsenopyrite is similar to a proposed mechanism for pyrite oxidation,[25,26] whereby the sulfur at the mineral surface forms a series of sulfoxy anions culminating in thiosulfate, which is then released to solution:

$$2FeAsS(s) + 14Fe^{3+}(aq) + 9H_2O \rightarrow$$
$$16Fe^{2+}(aq) + S_2O_3^{2-}(aq) + 2H_3AsO_3(aq) + 12H^+(aq) \quad (3)$$
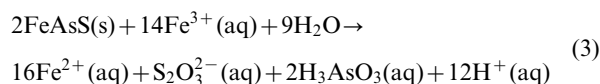
In this mechanism, every atom of sulfur liberated from the mineral proceeds through thiosulfate as an intermediate species. Thiosulfate ions liberated into solution can react subsequently *via* at least two pathways. In one pathway, the thiosulfate is oxidized in solution to sulfate:[25]

$$S_2O_3^{2-}(aq) + 8Fe^{3+}(aq) + 5H_2O \rightarrow 2SO_4^{2-}(aq) +$$
$$8Fe^{2+}(aq) + 10H^+(aq) \quad (4)$$
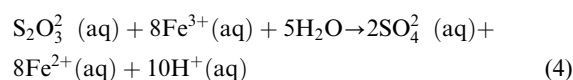
In this case, no elemental sulfur is formed.

In a second possible pathway, the thiosulfate could undergo a decomposition reaction in acidic solutions to form bisulfite, HSO_3^{2-}, and elemental sulfur:[27]

$$S_2O_3^{2-}(aq) + H^+(aq) \rightarrow HSO_3^-(aq) + S(s) \quad (5)$$

In the presence of ferric iron, the bisulfite in solution is oxidized to dithionate, $S_2O_6^{2-}$, and sulfate.[28]

Although the presence of elemental sulfur can be accounted for in the thiosulfate reaction scheme, this mechanism limits the maximum amount of elemental sulfur that may be formed.[17] Because all the reacted sulfur from arsenopyrite proceeds through thiosulfate in this proposed mechanism, and each molecule of thiosulfate yields one atom of elemental sulfur and one sulfite (SO_3^{2-}) ion through the decomposition reaction, at most 50% of the total reacted sulfur can be in the form of elemental sulfur. The results of our study, showing that well over 50% of the sulfur-containing reaction products is present as elemental sulfur after oxidation by ferric iron, indicate that the thiosulfate mechanism alone does not adequately describe the dissolution mechanism of arsenopyrite.

The exact details of how elemental sulfur forms on arsenopyrite are not known, however, the general scheme must involve the initial production of lower oxidation-state sulfur products such as elemental sulfur rather than the immediate progression to higher oxidation-state products such as sulfoxy anions. The buildup of sulfur on the mineral surface indicates that the oxidation of the sulfur species is the slowest step in the overall oxidation process, and that Fe and As are likely released into solution first. Since the sulfur layers can be many monolayers thick, the net release of arsenic is controlled by the rate at which the Fe and/or As sites are oxidized to water-soluble products (most likely Fe^{2+} and H_3AsO_3 or $H_2AsO_3^-$). Thus, we believe that oxidation initially produces a surface that might best be described as an excess of S^- ions; direct electron transfer from ferric iron then could produce a S^0 lattice. Subsequent nucleation would result in the formation of stable S_8 rings. Such a mechanism is supported by Buckley and Walker's surface studies of acid-leached arsenopyrite that revealed the presence of a sulfur-rich layer resembling a metal-deficient sulfide lattice.[29] Polysulfide intermediates, as

previously observed on oxidized pyrite surfaces,[30,31] may also play a role in these reactions.

Conclusion

Our results show that the amount of elemental sulfur found at the arsenopyrite surface cannot be accounted for by the decomposition of thiosulfate alone, and indicate that an additional direct pathway to the formation of elemental sulfur at the arsenopyrite surface must also be taken into account. Although it cannot be determined from this study whether all the sulfur proceeds through elemental sulfur and then is further oxidized to sulfoxy species or whether there are separate, parallel reaction pathways to these products, this work suggests that any summary of the reaction stoichiometry should include elemental sulfur as a major product. Additionally, the abundance of elemental sulfur has implications for understanding the roles of various microorganisms involved in the oxidation of sulfides. For example, the sulfur oxidizer *Thiobacillus caldus* is very efficient at removing the elemental sulfur layer that forms on arsenopyrite and other sulfide minerals during oxidative dissolution.[14] The abundance of elemental sulfur at the mineral surface is certainly a determining factor in the growth of such microbial communities.

Acknowledgements

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