

Kinetics of arsenopyrite oxidative dissolution by oxygen

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Abstract

We used a mixed flow reactor system to determine the rate and infer a mechanism for arsenopyrite (FeAsS) oxidation by dissolved oxygen (DO) at 25 °C and circumneutral pH. Results indicate that under circumneutral pH (6.3–6.7), the rate of arsenopyrite oxidation, $10^{-10.14 \pm 0.03} \text{ mol m}^{-2} \text{ s}^{-1}$, is essentially independent of DO over the geologically significant range of 0.3–17 mg L⁻¹. Arsenic and sulfur are released from arsenopyrite in an approximate 1:1 molar ratio, suggesting that oxidative dissolution by oxygen under circumneutral pH is congruent. Slower rates of iron release from the reactor indicate that some of the iron is lost from the effluent by oxidation to Fe(III) which subsequently hydrolyzes and precipitates. Using the electrochemical cell model for understanding sulfide oxidation, our results suggest that the rate-determining step in arsenopyrite oxidation is the reduction of water at the anodic site rather than the transfer of electrons from the cathodic site to oxygen as has been suggested for other sulfide minerals such as pyrite.

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1. Introduction

Arsenic has been linked to various diseases, including skin and bladder cancer (Smith et al., 2002). Elevated levels of arsenic have been found in natural waters in many areas around the world (Nordstrom, 2002; Smedley and Kinniburgh, 2002). While some arsenic pollution is associated with anthropogenic inputs, the more widespread sources are from weathering of arsenic-bearing sulfide minerals, such as arsenopyrite (FeAsS), orpiment (As₂S₃), and realgar (AsS), and arsenic-rich iron oxyhydroxides (Welch et al., 2000; Nordstrom, 2002; Nordstrom and Archer, 2003; Smedley and Kinniburgh, 2002). Elucidating the rates and mechanisms by which these arsenic-bearing minerals weather is an integral step to understanding arsenic retention and release in the environment.

The kinetics of orpiment and realgar oxidation by dissolved oxygen (DO) were studied by Lengke and Tempel (2002, 2003). At circumneutral pH and 25 °C, orpiment oxidation proceeded stoichiometrically (Lengke and

Tempel, 2002) and arsenic and sulfur were partially oxidized during the experiment, producing arsenite as the dominant arsenic species and several intermediate sulfur species. Similar to orpiment, oxidation of realgar yielded arsenite as the dominant arsenic species in solution (Lengke and Tempel, 2003). Results from these two series of experiments aid in delineation of the mechanism of arsenic sulfide oxidation, which bears some similarity to oxidation of other sulfide minerals. Specifically, the reaction order of realgar and orpiment oxidation with respect to DO (0.3–0.5) is similar to pyrite oxidation (0.5) (Williamson and Rimstidt, 1994), thus it is possible that orpiment and realgar oxidation shares the same rate-limiting step as pyrite—transfer of electrons from the mineral to the oxidant.

There have been a variety of studies addressing the kinetics of arsenopyrite oxidation by ferric iron at low pH (Gagen, 1987; Rimstidt et al., 1994; Fernandez et al., 1996; Breed et al., 1997; Ruitenberg et al., 1999; Yunmei et al., 2004). These previous studies have demonstrated reaction orders for oxidation of arsenopyrite by Fe(III) to range between 0.41 (Yunmei et al., 2004) and 0.98 (Rimstidt et al., 1994). However, very few data have been collected to evaluate arsenopyrite oxidation kinetics under circumneutral pH. At the initial stages of oxidation, both

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the mineral surface and the bulk porewater environment will be at near neutral pH, conditions under which Fe(III) has low solubility and oxygen will be the most important oxidant.

The main objectives of this study were to obtain a laboratory rate and infer a potential mechanism and rate-determining step for arsenopyrite oxidation under circumneutral pH conditions with dissolved oxygen as the oxidant. Results of this study are important not only for improving the database of weathering characteristics of arsenic-bearing minerals, but also for predicting release of different forms of arsenic from arsenopyrite weathering in field settings.

2. Materials and methods

2.1. Preparation of arsenopyrite

The arsenopyrite used in these experiments was from the Noche Buena mine in Zacatecas, Mexico. The average chemical formula for arsenopyrite was determined to be $\text{Fe}_{1.02}\text{As}_{0.95}\text{S}_{1.03}$ based on electron microprobe analysis. The sample was crushed in a mortar and pestle and the 60–80 mesh fraction (177–250 μm) diameter was retained for use in the experiment. Scanning electron microscopy (SEM) analysis of the powder revealed the presence of quartz which was removed by gravity separation with water.

Following sieving, the arsenopyrite was rinsed with 75% ethanol and placed in a sonicator for several minutes to remove ultrafine particles adhering to the surface of the mineral. The supernatant was decanted and the procedure was repeated until the supernatant was clear. The arsenopyrite was then dried for approximately 1 h at 50–60 °C and stored in a desiccator. Brunauer, Emmet, and Teller (BET) surface area analysis was conducted using a NOVA Quantachrome 1000 with nitrogen adsorption; the average specific surface area of the arsenopyrite was calculated to be 0.0388 $\text{m}^2 \text{g}^{-1}$.

2.2. Mixed flow reactor system

The oxidative dissolution rate of arsenopyrite under varying oxygen conditions and circumneutral pH was determined using an internally stirred mixed flow reactor system. Mixed flow reactors are advantageous compared to batch reactors because they measure rates directly, thereby eliminating the need to differentiate the concentration versus time data produced by batch reactors (Weissbart and Rimstidt, 2000). In these experiments, 1.00 g of arsenopyrite sample was confined between two nested o-rings in the reactor and held in place by nylon mesh attached to the outside of the o-rings with styrene glue. Viton tubing was used for the feed and effluent tubing in order to limit oxygen exchange with the atmosphere.

In each experiment, varying DO concentrations were established by bubbling feed solution (0.01 M NaCl) with

different oxygen concentrations (100% N_2 , air, 60% O_2 ; Table 1). Because the feed solution tank and tubing are slightly gas permeable, the actual oxygen saturation achieved in the feed solution was lower than would be expected in a closed system. For example, bubbling 60% O_2 gas into the solution yielded a maximum DO concentration of 17.1 mg L^{-1} , which is lower than the 24.2 mg L^{-1} predicted by Henry's law. However, for the purposes of these experiments, it was not necessary to achieve specific DO saturations. Instead, the goal was to maintain a constant value throughout each experiment and to measure rates over a range of DO conditions by performing different trials. The feed solution pH was not buffered and varied between 5.7 and 7.7 (Table 1).

After bubbling, the feed solution was pumped through the reactor, kept at constant temperature through immersion in a 25 °C water bath, at a rate of $0.325 \pm 0.006 \text{ mL min}^{-1}$. Upon leaving the reactor, the effluent continued through DO and pH electrode reservoirs and was collected in 10 mL acid-washed glass test tubes by a fraction collector set to change tubes at 30-min intervals. Experiments were run for approximately 24 h. Two tubes (representing 1 h) were preserved for chemical analysis: the first was preserved with HNO_3 for total arsenic, iron, and sulfur analyses, and the second was preserved with EDTA for arsenic speciation.

2.3. Analytical methods

Dissolved oxygen and pH measurements were recorded for the feed solution and effluent using an Orion DO probe (Model 081010), Orion pH meter (Model 8102BN), and a laptop computer equipped with Orion Sensorlink software. DO and pH values for the effluent were collected every 10 min throughout the experiment. Temperature in the water bath was monitored and maintained at 25 ± 0.2 °C.

Iron and sulfur concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), conducted using a SpectroFlame Modula Tabletop instrument. Detection limits for iron and sulfur were 3 and 11 $\mu\text{g L}^{-1}$, respectively. Sulfur (as sulfate) was also initially measured by using ion chromatography (Dionex DX 120); comparison with the ICP-AES results revealed that >95% of the effluent sulfur was present as sulfate. Arsenic concentrations were determined by graphite furnace atomic absorption spectroscopy (GFAAS) using a Varian Spectra 220Z with Zeeman background correction. The detection limit for arsenic was 2 $\mu\text{g L}^{-1}$. Arsenic speciation (arsenite and arsenate) was achieved by strong anion exchange column separation, followed by GFAAS analysis. The separation involves eluting a sample through a column wherein arsenite passes through the column while arsenate is retained on the column and extracted separately with HNO_3 (Le et al., 2000; Garbarino et al., 2002). Samples for arsenic speciation were analyzed within 3 days of collection. Testing of the speciation

Table 1
Experimental conditions and results

Gas	Flow rate (mL min ⁻¹)	Feed solution			Steady-state effluent				
		pH	DO (mg L ⁻¹)	log DO (mol L ⁻¹)	Time (h)	pH	log DO (mol L ⁻¹)	log <i>r</i> _{As} (mol m ⁻² s ⁻¹)	log <i>r</i> _S (mol m ⁻² s ⁻¹)
100% N ₂	0.325	7.6	0.5	-4.81	15	6.33	-4.81	-10.16	-10.14
					17	6.34	-4.81	-10.15	-10.14
					19	6.31	-4.9	-10.17	-10.12
					21	6.28	-4.9	-10.14	-10.10
					23	6.38	-4.73	-10.18	-10.10
100% N ₂	0.328	7.5	0.3	-5.03	15	6.33	-5.03	-10.11	-10.13
					17	6.41	-5.03	-10.13	-10.15
					19	6.41	-5.03	-10.15	-10.15
					21	6.58	-5.03	-10.00	-10.05
					23	6.59	-5.03	-10.05	-10.12
Air	0.335	5.7	6	-3.75	15	6.35	-3.69	-10.27	-10.28
					17	6.27	-3.69	-10.28	-10.30
					19	6.27	-3.69	-10.23	-10.30
					21	6.30	-3.69	-10.25	-10.34
					23	6.30	-3.69	-10.26	-10.30
Air	0.333	5.8	6.3	-3.74	15	6.29	-3.74	-10.09	-10.02
					17	6.35	-3.73	-10.04	-10.08
					19	6.28	-3.74	-10.09	-10.12
					21	6.33	-3.73	-10.13	-10.16
					23	6.36	-3.73	-10.16	-10.16
Air	0.318	6.3	5.5	-3.71	15	6.74	-3.72	-10.04	-10.02
					17	6.71	-3.72	-10.02	-10.02
					19	6.71	-3.71	-10.08	-10.06
					21	6.73	-3.71	-10.15	-10.20
					23	6.65	-3.71	-10.20	-10.17
60% O ₂	0.323	6.8	16.5	-3.67	15	6.59	-3.29	-10.13	-10.16
					17	6.65	-3.31	-10.18	-10.15
					19	6.59	-3.3	-10.20	-10.17
					21	6.64	-3.28	-10.26	-10.25
					23	6.58	-3.28	-10.21	-10.30
60% O ₂	0.320	7.7	17.1	-3.62	15	6.64	-3.27	-10.06	-10.16
					17	6.65	-3.27	-10.06	-10.16
					19	6.68	-3.26	-10.06	-10.23
					21	6.63	-3.27	-10.05	-10.20
					23	6.63	-3.27	-10.01	-10.16

technique documented >95% recovery of arsenite and arsenate species.

2.4. Rate calculations, error analysis, and statistical analysis

Steady-state release rates for iron, arsenic, and sulfur were calculated from the mixed flow reactor experimental data using the equation:

$$r_i = \frac{m_i r_f}{MA}, \quad (1)$$

where r_i is the release rate of i in mol m⁻² s⁻¹, m_i is the molality of i (mol kg⁻¹) in the effluent solution, r_f is the rate of feed solution in kg s⁻¹, M is the mass of FeAsS (g), and A is the specific surface area of FeAsS (m² g⁻¹). It was expected that the arsenopyrite oxidation rate would be a function of DO and pH, similar to pyrite (Williamson and Rimstidt, 1994) and other arsenic sulfides (Lengke and Tempel, 2002, 2003) and thus the rate law with respect to species i would be of the form:

$$r = (Ak)a_{\text{O}_2}^m a_{\text{H}^+}^n, \quad (2)$$

which can be transformed to logarithmic form:

$$\log r_i = \log k' + m \log a_{\text{O}_2} - n \log a_{\text{H}^+}, \quad (3)$$

where k is the rate constant in mol m⁻² s⁻¹, a_i is the activity of i in mol kg⁻¹, k' is the the apparent rate constant = Ak in mol s⁻¹, and m and n are reaction orders for O₂ and H⁺, respectively.

The reaction progress variable for arsenopyrite oxidation was determined through inspection of the data. Although sulfur is the more common choice of reaction progress variable for sulfide mineral oxidation due to its conservative behavior (McKibben and Barnes, 1986), arsenic was chosen in this study for two reasons. First, the method used to analyze arsenic concentrations, GFAAS, is more accurate for low (<100 μg L⁻¹) arsenic concentrations than the ICP methods used to measure sulfur concentrations. Second, pairwise t test statistical analyses showed no significant difference between the arsenic and the sulfur release rates. Thus, we chose to use the arsenic release rate to represent the rate of arsenopyrite oxidation by oxygen.

For this investigation, steady state was defined as beginning at the point in time where the change between successive concentration measurements was less than 15%. For all experiments, steady state was reached at or before 15 h. Linear regression methods were used to calculate values of k , m , and n using the experimental data. Only full data sets (sampling times where arsenic, iron, sulfur, pH, and DO were all measured, $n = 35$) were used in the linear regression.

The accuracy of each rate measurement was examined using the error propagation method of Taylor (1982):

$$\frac{\delta r}{r} = \sqrt{\left(\frac{\delta m_{As}}{m_{As}}\right)^2 + \left(\frac{\delta r_f}{r_f}\right)^2 + \left(\frac{\delta A}{A}\right)^2}, \quad (4)$$

where $\delta r/r$ is the fractional error in the rate, $\delta m_{As}/m_{As}$ is the fractional error in the measured concentration of arsenic measured in effluent, $\delta r_f/r_f$ is the fractional error in the measured feed rate, and $\delta A/A$ is the fractional error in the measured surface area. For these experiments, fractional errors were estimated as follows: concentration of arsenic (5%), feed rate (2%), and surface area (10%). The mass of arsenopyrite was accurate within 0.01 g (<1%) and was thus not included in the error propagation calculations. From these estimates of experimental error, the uncertainty in the arsenic rate is approximately 11%.

Because the mixed flow reactor experiments yield time-series data, where many measurements of concentrations (and thus rate estimates) are made over time within an individual experiment, a repeated measures analysis of variance (ANOVA) was conducted to determine if there were between-subjects (DO) effects, within-subjects (time) effects, and interactions between time and DO. For the among-subject effects, repeated measures showed that DO was not a significant main effect ($p > 0.05$), indicating no significant differences of r_{As} across time. For the within-subjects effects, Wilks' Lambda statistic ($p > 0.05$) showed that within each DO level, there was no significant variation in r_{As} with time. Finally, DO and time did not interact significantly ($p > 0.05$), indicating that the influence of DO was not dependent upon time. Results of this repeated measures analysis support the use of time-series data in our calculations of the rate constant for arsenopyrite oxidation and emphasize the independence of rate on ambient levels of oxygen availability.

3. Results and discussion

3.1. Arsenopyrite dissolution behavior

The trends of arsenic and sulfur concentrations in the effluent versus time for all DO conditions reveal rapidly decreasing release rates (Fig. 1), as is typical for most mineral dissolution until steady state is reached. Although the sample was sonicated, thus removing fines from the surface, limited surface oxidation may have occurred during the drying process. Additionally, there may have been

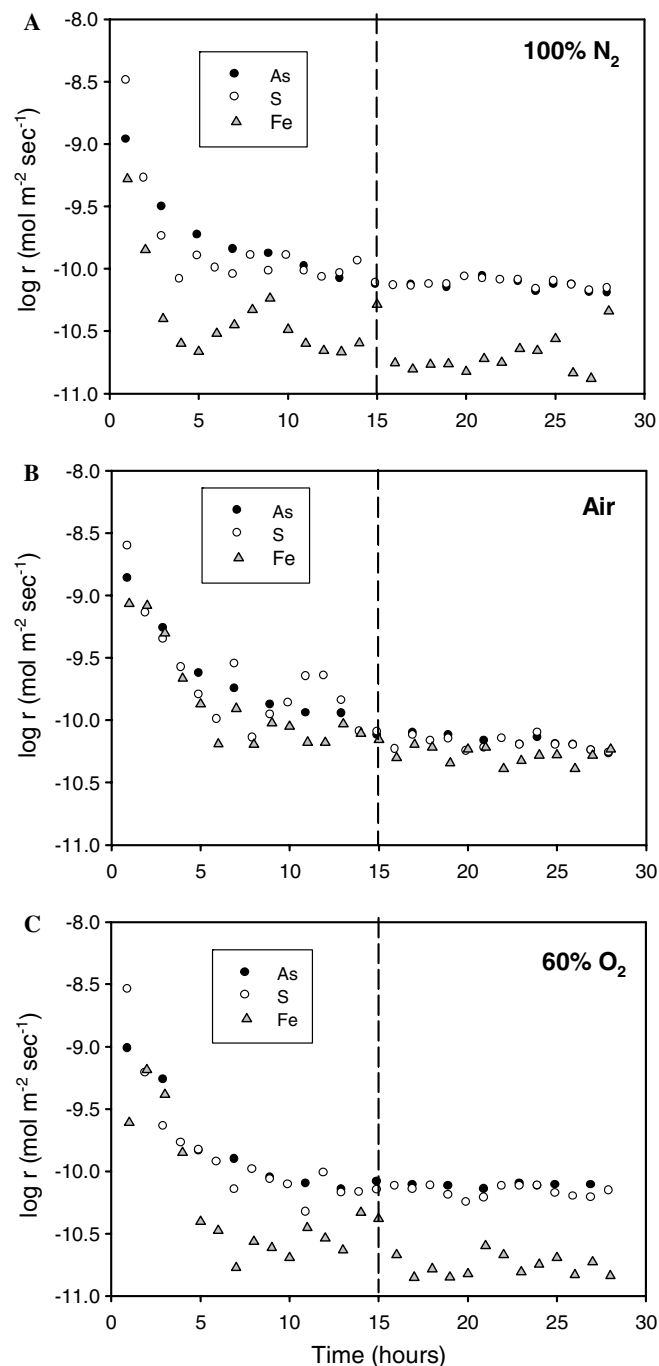


Fig. 1. Average log release rates versus time for As, S, and Fe for experiments equilibrated with (A) N_2 , (B) air, and (C) 60% O_2 . Dashed line shows 15 h, the time at which steady state is reached.

preferential dissolution at cracks or other defects on the mineral surface during the initial stages of the experiments, as was observed by Borda et al. (2004). After 15 h, which was determined to be steady-state conditions, concentrations of all species stabilized.

The equimolar (1:1) concentrations of arsenic and sulfur in the effluent (Fig. 2) and the statistical similarity (pairwise t test) of the arsenic and sulfur release rates suggest that dissolution of arsenopyrite occurs stoichiometrically.

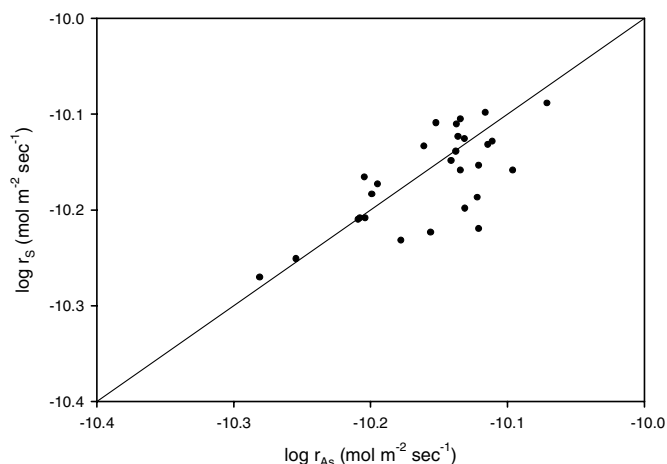


Fig. 2. Comparison of steady-state sulfur to arsenic release rates for the arsenopyrite oxidation experiments ($n = 35$). Line represents equimolar (1:1) release.

Pairwise t test analysis and visual inspection of the data (Fig. 1) show that steady-state iron release rates are significantly lower than arsenic (or sulfur) release rates, indicating that some iron is being attenuated within the experimental system. At the DO and pH conditions of the experiments, it is likely that the released iron (present in ferrous form) undergoes oxidation and precipitates as iron oxyhydroxides, either on the arsenopyrite surface or on the reactor, as has been shown in spectroscopic studies of arsenopyrite surfaces undergoing oxidation by oxygen (Richardson and Vaughan, 1989; Nesbitt et al., 1995). Arsenic has a strong adsorption affinity for iron oxyhydroxides (e.g., Stollenwerk, 2003) and precipitation of iron oxyhydroxides could potentially cause arsenic loss from solution. However, our results reveal no preferential attenuation of arsenic with respect to sulfur, suggesting that significant arsenic sorption to secondary iron oxyhydroxides did not occur in these experiments, that arsenic and sulfur adsorption occurred at the same rate, or that the iron oxyhydroxide surface area was so low that only a negligible amount of arsenic was adsorbed.

3.2. Arsenopyrite oxidation kinetics

Multiple linear regression of the entire arsenopyrite data set ($\log r_{As}$, pH, $\log m_{O_2}$) revealed a slight dependence of the rate on pH, but due to the very narrow range of pH of solution effluent (6.3–6.7), the dependence was suspected to be an artifact of the regression. Thus, a single linear regression of $\log r_{As}$ against $\log m_{O_2}$ was conducted to determine the dependence of the oxidation rate on oxygen. Results of the regression, including the intercept (k) and the coefficient for the O_2 term (m), along with the standard error for each coefficient, are shown in Table 2. Also included are regression coefficients from multiple linear regression for the oxidation of pyrite (Williamson and Rimstidt, 1994), realgar (Lengke and Tempel, 2003), and orpiment (Lengke and Tempel, 2002) regressed against pH and $\log m_{O_2}$.

Regressing $\log r_{As}$ against $\log m_{O_2}$ yields a value of k for arsenic release of $10^{-10.17(\pm 0.08)}$ mol m⁻² s⁻¹ and an m coefficient for the O_2 term of $-0.01(\pm 0.02)$ (Table 2). Because the coefficient m of the oxygen term is not significantly different from zero ($p = 0.6745$), suggesting that oxygen exerts a negligible influence on the oxidation rate, the rate law for arsenopyrite oxidation by oxygen at near-neutral pH can be expressed as the average rate for arsenic release ($\pm 95\%$ confidence interval):

$$r_{As} = r_{Aspy,O_2} = 10^{-10.14(\pm 0.03)} \quad (5)$$

Leverage plots were constructed from the linear regression data to show the influence of the multiple independent variables (pH, $\log m_{O_2}$) on the overall model-dependent variable (rate) for arsenopyrite and other sulfides. The pH leverage plot (Fig. 3A) shows the influence of pH on the oxidation rate of pyrite, realgar, and orpiment held at a constant DO concentration of 5 mg L⁻¹ ($10^{-3.8}$ M). Oxidation of the arsenic sulfides, realgar and orpiment, shows the strongest pH dependence (reaction orders of 0.26 and 0.46, respectively) while pyrite oxidation has weaker pH dependence (reaction order of 0.11) (Table 2). Due to the narrow range of pH tested in this study, the arsenopyrite data were not regressed against pH but are shown on the

Table 2
Coefficients (\pm SE) for the generalized rate laws of sulfide oxidation by oxygen (Eq. (3)) derived from linear regression

Oxidation rate (r) (mol m ⁻² s ⁻¹)	Intercept (k)	DO coefficient (m) (mol L ⁻¹)	p	pH coefficient (n)	p
Aspy ^a	-10.17 (± 0.08)	-0.01 (± 0.02)	0.6745	—	—
Aspy ^b	-10.14 (± 0.03)	—	—	—	—
Pyrite ^c	-8.20 (± 0.06)	0.50 (± 0.02)	<0.0001	0.11 (± 0.01)	<0.0001
Realgar ^d	-9.39 (± 0.34)	0.55 (± 0.08)	0.0001	0.26 (± 0.04)	<0.0001
Orpiment ^e	-12.17 (± 0.48)	0.24 (± 0.11)	0.0558	0.46 (± 0.04)	<0.0001

Values of $p < 0.01$ indicate that the coefficient is statistically significant.

^a This study ($n = 35$, $R^2 = 0.02$). Due to narrow pH range (6.3–6.7), rates were not regressed against pH.

^b This study ($n = 35$), average of all arsenic release rates ($\pm 95\%$ confidence interval).

^c Williamson and Rimstidt (1994) ($n = 56$; $R^2 = 0.90$).

^d Lengke and Tempel (2003) ($n = 13$; $R^2 = 0.84$), using steady-state As rate data at 25 °C.

^e Lengke and Tempel (2002) ($n = 11$, $R^2 = 0.94$) using steady-state As rate data at 25 °C.

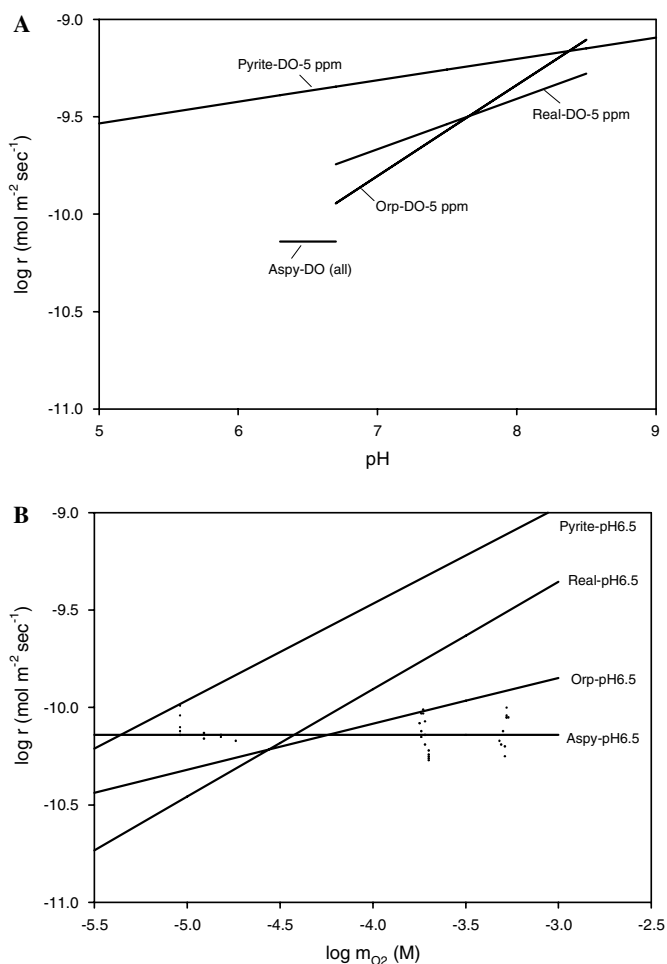


Fig. 3. Leverage plots showing influence of independent variables pH and DO on the model-dependent variable, sulfide oxidation rate. (A) Influence of pH on oxidation rates of arsenopyrite, pyrite, realgar, and orpiment, with DO of 5 mg L^{-1} ($10^{-3.8} \text{ M}$). Extent of regression lines reflects pH ranges in which experiments were conducted. (B) Influence of $\log m_{\text{O}_2}$ on oxidation of pyrite, realgar, orpiment, and arsenopyrite (both regression line and data points shown) at pH 6.5. Data collected from the following sources: arsenopyrite by dissolved oxygen (this study), pyrite (Williamson and Rimstidt, 1994), realgar (Lengke and Tempel, 2003), and orpiment (Lengke and Tempel, 2002).

plot at the pH range of the experiments for comparison. However, previous work in the metallurgical literature has documented that arsenopyrite oxidation by oxygen is greatly enhanced under alkaline conditions (e.g. Nicol and Guresin, 2003), indicating a pH dependence of this reaction at high pH.

The leverage plot of $\log r$ versus $\log m_{\text{O}_2}$ (Fig. 3B) shows the influence of oxygen concentration on the oxidation rate of pyrite, realgar, orpiment, and arsenopyrite at pH 6.5. Inspection of this plot shows the strong oxygen dependence of oxidation of pyrite and realgar (reaction orders of 0.50 and 0.55, respectively) and moderate dependence for orpiment (reaction order of 0.24) (Table 2). In contrast, the oxidation rate of arsenopyrite shows no influence of oxygen over the range of m_{O_2} from $10^{-3.5}$ to $10^{-5.5} \text{ M}$. Calculation of the oxidation rate at near-neutral pH for different

oxygen conditions reveals that at low oxygen ($10^{-5.5} \text{ M}$, or 0.1 mg L^{-1}) concentrations, typical of reducing groundwater, arsenopyrite oxidation is as fast as pyrite oxidation and is 0.25–0.5 order of magnitude faster than orpiment and realgar oxidation, respectively. As oxygen increases to $10^{-4.5} \text{ M}$ (1 mg L^{-1}), typical of moderately reducing groundwater, the oxidation rates of arsenopyrite, realgar, and orpiment are equal, and are 0.5 order of magnitude lower than pyrite. At high oxygen ($10^{-3.5} \text{ M}$ or 10 mg L^{-1}), not typical in groundwater but in low temperature surface water in contact with the atmosphere, the rate of pyrite oxidation is a full order of magnitude higher than the arsenopyrite rate.

3.3. Arsenic speciation

Spectroscopic data collected during arsenopyrite oxidation experiments (Richardson and Vaughan, 1989; Nesbitt et al., 1995; Nesbitt and Muir, 1998) show complex changes in the speciation of iron, sulfur, and arsenic on the arsenopyrite surface during oxidation. In unaltered arsenopyrite, arsenic occurs as As(0) or As(-I) but after the surface has been oxidized, a variety of oxidation states of arsenic are observed on the surface, including As(-I), As(I), As(III), and As(V) (Richardson and Vaughan, 1989; Nesbitt et al., 1995; Foster et al., 1998; Nesbitt and Muir, 1998; Reynolds et al., 1999; Schaufuss et al., 2000). Although a variety of oxidation states occurs on the surface, for redox conditions prevalent in natural water, the dominant arsenic species are As(III) and As(V).

To examine the extent of arsenic oxidation within the reactor assembly in the absence of arsenopyrite, we conducted a control experiment, in which As(III) in air-saturated 0.01 M NaCl solution was pumped through the system and the effluent solution was analyzed for As(III) and As(V). Results showed that 40% of the initial As(III) in feed solution was oxidized to As(V) during transport through the reactor. Correcting for this reactor oxidation, the percentage of As(V) as total arsenic in effluent for all experiments at steady state ranged from 20 to 45% (Fig. 4). The level of DO impacted arsenic speciation, with higher DO concentrations resulting in higher As(V) effluent concentrations.

Several other studies have examined arsenic speciation during oxidation of arsenic-bearing minerals. In a study by Yunmei et al. (2004) where arsenopyrite was oxidized by ferric iron under low pH, the factors exerting the strongest controls on effluent arsenic speciation were the type and concentration of the oxidant. Use of ferric sulfate resulted in effluent As(III) concentrations >93%, whereas use of ferric chloride yielded predominantly As(V) (>99% after 5 h). Concentration of Fe(III) also impacted speciation; at low concentrations of Fe(III), As(III) was the dominant species (89% of total). As Fe(III) concentrations were increased, the oxidation of As(III) to As(V) also increased, resulting in 53% As(III) at the end of the experiment. Lengke and Tempel (2002, 2003) examined arsenic specia-

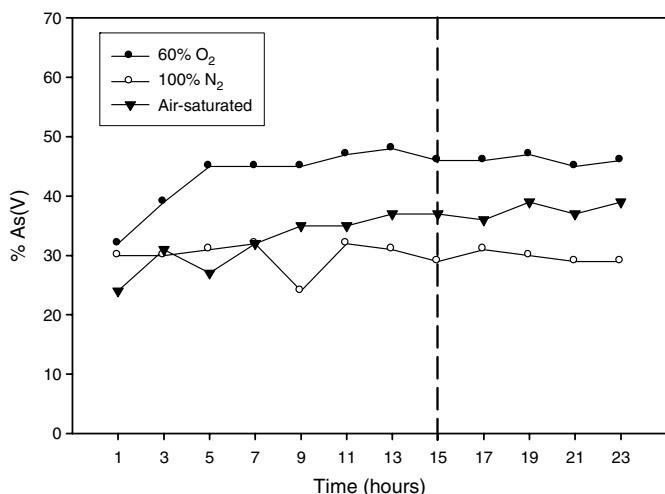


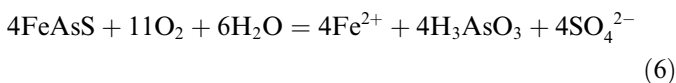
Fig. 4. Percent of As(V) of total arsenic over time for experiments equilibrated with 100% N₂, air, and 60% O₂. Results have been corrected for oxidation occurring in the reactor in the absence of FeAsS. Dashed line at 15 h shows location of steady state.

tion during oxidation of realgar and orpiment by dissolved oxygen; results showed mixtures of As(III) and As(V) in effluent, with a ratio of 60% As(III) to 40% As(V) similar to our results.

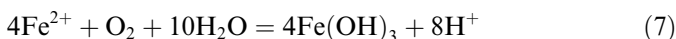
Comparing our results with Lengke and Tempel (2002, 2003) and Yunmei et al. (2004), it becomes clear that oxidant type impacts solution arsenic speciation, as shown by the different results observed in effluent from oxidation of arsenic sulfides by oxygen (mixtures of As(III) and As(V)), ferric sulfate (all As(III)), and ferric chloride (all As(V)). The impact of oxidant concentration is also apparent, with higher concentrations resulting in higher As(V)/As(III) ratios.

3.4. Arsenopyrite oxidation reactions

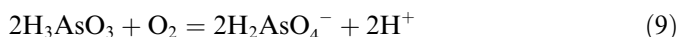
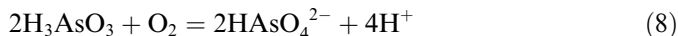
Our experimental results (Table 2) show a modest decrease of pH (0.5–1 pH unit) in effluent of the low oxygen (100% N₂) and high oxygen (60% O₂) equilibrated solutions reacted with arsenopyrite. Craw et al. (2003) observed similar results in laboratory experiments of arsenopyrite oxidation; pH decreased only slightly in the experiments conducted at near-neutral pH. These results suggest the series of oxidation reactions below, starting with the oxidation of arsenopyrite by oxygen at near-neutral pH, where As(III) is present as the uncharged ion H₃AsO₃:



Although this reaction does not generate acidity, subsequent secondary reactions can yield protons to solution. First, the ferrous iron released from reaction (6) can be oxidized, forming iron oxyhydroxide:



The As(III) produced in reaction (6) can be further oxidized to As(V). Because the pK_{a2} of As(V) is 6.98, at near-neutral pH, arsenite oxidation to As(V) will yield HAsO₄²⁻ and H₂AsO₄⁻ in approximately equal concentrations via the following reactions:



As shown by our experimental results, iron oxidation (Fig. 1) and As(III) oxidation (Fig. 4) are only partially complete. The extent of oxidation of these species in the laboratory will be experimentally controlled, as some oxidation may occur in solution and will be affected by time of contact with the atmosphere, flow rate, oxidant concentration, and photochemical reactions. Variability of reaction extent for iron and As(III) oxidation will also occur in the field. Because the oxidation of iron and As(III) releases protons to solution, the pH of water interacting with arsenopyrite will likely be moderately depressed. However, the actual pH will depend on the extent of those secondary oxidation reactions, which is in turn controlled by site hydrologic and biogeochemical conditions.

3.5. Mechanistic implications

The finding that arsenopyrite oxidation rate has essentially no dependence on oxygen is surprising given that oxidation of other sulfides shows oxygen dependence (Williamson and Rimstidt, 1994; Lengke and Tempel, 2002, 2003). We believe that the best explanation is offered by consideration of electrochemical cell model, which is often used to describe sulfide oxidation (Williamson and Rimstidt, 1994; Rimstidt and Vaughan, 2003). In this model, the oxidation of arsenopyrite can be viewed as a series of three consecutive steps. Any of these three steps could be the rate-limiting step for the overall reaction.

The first step involves donation of electrons from a cathodic site to the oxidant. This is the rate-determining step for pyrite oxidation, as many studies have shown that the oxidation rate is controlled by the concentration of the oxidant (e.g., Brown and Jurinak, 1989; Rimstidt and Vaughan, 2003). Because our results show that the overall rate is independent of oxygen concentration, the cathodic step is not the rate-determining step for this reaction.

The second step, which involves electron transfer from the anodic site to replace lost electrons at the cathodic site, is controlled by the mineral's electrical resistivity. The measured electrical resistivity value for arsenopyrite (0.03 Ω cm) is within the range of the resistivity measured for pyrite (0.005 to 5 Ω cm) (Vaughan and Craig, 1978). The similar values of resistivity, and the fact that electron transfer is not the rate-determining step for pyrite, suggest that this second step is also not the rate-determining step for arsenopyrite oxidation by oxygen.

We conclude by process of elimination that the rate-determining step for oxidation of arsenopyrite must be the

third step. This step involves the generation of electrons at the anodic site, where oxygen from water attaches to arsenic and sulfur species. Forming sulfate from disulfide or sulfide-sulfur involves removal of seven to eight electrons, respectively, while forming As(III) or As(V) from As(-I) involves removal of four or six electrons, respectively. The multi-step oxidation of arsenic and sulfur species is challenging to study because the oxidation intermediates are transient and are difficult to measure on surfaces and in solution. Even spectroscopic methods have difficulty observing these oxidation states, as ex situ methods require removal of samples from the experimental conditions into air or high vacuum. Additional experiments using in situ spectroscopic methods, similar to the approach outlined in Borda et al. (2004), would provide further clarification of the mechanisms controlling the arsenopyrite oxidation process.

4. Conclusions

The rate of arsenopyrite oxidation by oxygen at circum-neutral pH was determined using mixed flow reactors under varying oxygen conditions. Oxidation of arsenopyrite released arsenic, as a mixture of arsenite (60%) and arsenate (40%), and sulfur, as sulfate, in approximately 1:1 molar ratio, suggesting congruent dissolution. Our results demonstrate that the rate of arsenopyrite ($r_{\text{Aspy},\text{O}_2} = 10^{-10.14 \pm 0.03} \text{ mol m}^{-2} \text{ s}^{-1}$) is not oxygen dependent as has been observed for other sulfide minerals, which suggests a different mechanism of arsenopyrite oxidation by oxygen at circumneutral pH. We propose that the rate-determining step is likely the slow reduction of water at anodic sites on the arsenopyrite surface, but further experimentation is required to adequately test this hypothesis.

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