Non-linear Hydroxyl Radical Formation Rate in Dispersions Containing Mixtures of Pyrite and Chalcopyrite Particles

Jasmeet Kaur, Martin A. Schoonen[#]

Department of Geosciences, Stony Brook University, Stony Brook, NY-11794-2100, USA

ABSTRACT

The formation of hydroxyl radicals was studied in mixed pyrite-chalcopyrite dispersions in water using the conversion rate of adenine as a proxy for hydroxyl radical formation rate. Experiments were conducted as a function of pH, presence of phosphate buffer, surface loading, and pyrite-to-chalcopyrite ratio.

The results indicate that hydroxyl radical formation rate in mixed systems is non-linear with respect to the rates in the pure endmember dispersions. The only exception is a set of experiments in which phosphate buffer is used. In the presence of phosphate buffer, the hydroxyl radical formation is suppressed in mixtures and the rate is close to that predicted based on the reaction kinetics of the pure endmembers.

The non-linear hydroxyl radical formation in dispersions containing mixtures of pyrite and chalcopyrite is likely the result of two complementary processes. One is the fact that pyrite and chalcopyrite form a galvanic couple. In this arrangement, chalcopyrite oxidation is accelerated, while pyrite passes electrons withdrawn from chalcopyrite to molecular oxygen, the oxidant. The incomplete reduction of molecular oxygen leads to the formation of hydrogen peroxide and hydroxyl radical. The galvanic coupling appears to be augmented by the fact that chalcopyrite generates a significant amount of hydrogen peroxide upon dispersal in water. This

[#] Corresponding author, email: martin.schoonen@stonybrook.edu

hydrogen peroxide is then available for conversion to hydroxyl radical, which appears to be facilitated by pyrite as chalcopyrite itself produces only minor amounts of hydroxyl radical. In essence, pyrite is a “co-factor” that facilitates the conversion of hydrogen peroxide to hydroxyl radical. This conversion reaction is a surface-mediated reaction.

Given that hydroxyl radical is one of the most reactive species in nature, the formation of hydroxyl radicals in aqueous systems containing chalcopyrite and pyrite has implications for the stability of organic molecules, biomolecules, the viability of microbes, and exposure to dust containing the two metal sulfides may present a health burden.

39 1. INTRODUCTION

40 Pyrite, FeS₂, and chalcopyrite, CuFeS₂, are both abundant on Earth and are often found
 41 together in nature. Besides their coexistence in nature, it has been well established in the field of
 42 metallurgy that pyrite and chalcopyrite form a galvanic couple (Berry et al., 1978; Dixon et al.,
 43 2008; Majuste et al., 2012; Mehta and Murr, 1983). The galvanic coupling between the two
 44 minerals hinges on their semiconducting properties (Xu and Schoonen, 2000) and the fact that
 45 the rest potential of each of the materials differs. The rest potential is the potential at which no
 46 net current flows between an electrode made out of the metal sulfide and the solution it is placed
 47 in. Hence, rest potentials depend on solution composition. The rest potential relative to
 48 Standard Hydrogen Electrode in 1N sulfuric acid for chalcopyrite is 0.52V and that for pyrite is
 49 0.63V at 20° C (Koleini et al., 2010). This difference in rest potential effectively organizes a
 50 system with coexisting pyrite and chalcopyrite into one in which pyrite will donate electrons to
 51 the aqueous oxidant and chalcopyrite replenishes these electrons. In this process, chalcopyrite
 52 oxidizes and releases metal ions solution (reaction 1).

54 Pyrite acts as an inert electrode and passes electrons derived from chalcopyrite to the oxidant.
 55 Hence, chalcopyrite preferentially oxidizes and pyrite undergoes little or no reaction in a
 56 galvanically coupled pyrite-chalcopyrite system. This effect is exploited in the extraction of
 57 copper from low-grade ore (Koleini et al., 2011; Koleini et al., 2010; Nazari et al., 2011).

58 The notion of a galvanically coupled pyrite-chalcopyrite system hinges on the ability of
 59 electrons to be passed from chalcopyrite to pyrite. The electron transfer between the two phases

is expected to be unimpeded in ore or ore concentrate in which the two metal sulfides share grain boundaries or are intergrown. Copper leaching experiments conducted on dispersions with mixtures of separate pure chalcopyrite and pyrite particles indicate that even in dispersions the two metal sulfides establish a galvanic couple. Not only do these experiments show the preferential leaching of copper, but they also show that the copper leaching rate reaches a maximum with pyrite-to-chalcopyrite particle loading ratios in excess of 4 (Koleini et al., 2010).

If dissolved molecular oxygen is the oxidant in a pyrite-chalcopyrite dispersion, it will be reduced. This process is often represented by the following overall reaction:

Reaction 2 combines at a minimum two elementary electron transfer steps as the number of electrons that can be transferred in a single step is limited to a maximum of two (Schoonen and Strongin, 2005). As a result, partial reduction products are expected to form in air-saturated metal sulfide dispersions (Fig. 1). For example, the partial reduction of molecular oxygen in dispersions of pyrite has been shown to lead to the formation of hydrogen peroxide (reaction 3) and hydroxyl radical (reaction 4) (Cohn et al., 2006b; Cohn et al., 2005; Jones et al., 2013b; Schoonen et al., 2010). The reduction of hydrogen peroxide (reaction 4) is often coupled with the oxidation of ferrous iron, which is known as the Fenton reaction (reaction 5). This reaction can take place on the metal sulfide surface or in solution (Fig. 1). Hydroxyl radicals are highly reactive and will rapidly extract an electron from any organic molecule, ferrous iron, or reduced sulfur species and form hydroxide ion in the process (reaction 6), completing the 4-electron transfer per dissolved oxygen molecule (reaction 2).

Ferric iron is an alternative electron acceptor in chalcopyrite-pyrite dispersions. Ferric iron is formed by the oxidation of ferrous iron generated by reaction 1. This oxidation step from ferrous to ferric iron requires the presence of dissolved molecular oxygen and also leads to the formation of partially reduced oxygen species.

The spontaneous formation of hydrogen peroxide, H_2O_2 , and hydroxyl radicals, $\cdot\text{OH}$, in air-saturated dispersions of pyrite has implications for human health (Cohn et al., 2006a; Fubini and Fenoglio, 2007; Harrington et al., 2011; Plumlee and Morman, 2011; Silva et al., 2009; Silva et al., 2011), the stability of biomolecules (Cohn et al., 2004; Cohn et al., 2006c), the viability of bacteria (Friedlander et al., 2015; Williams and Haydel, 2010; Williams et al., 2011), and can be used to degrade persistent organic contaminants (Bae et al., 2013; Che et al., 2011; de Brito Benetoli et al., 2012; Feng et al., 2012; Matta et al., 2007; Matta et al., 2008; Pham et al., 2008; Wang et al., 2012; Wu et al., 2013; Wu et al., 2015; Zhang et al., 2015). In this study, we evaluate the effect of the coexistence of pyrite and chalcopyrite on the formation of hydroxyl radical. The rationale for this study is two-fold. If a system of dispersed pyrite and chalcopyrite is in fact galvanically coupled, the expectation is that pyrite will undergo little or no surface alteration as the overall system is oxidized. This will minimize or prevent formation of secondary Fe(III)-O-H products on the pyrite surface (Murphy and Strongin, 2009; Rosso et al., 1999; Usher et al., 2005) that have been shown to decompose hydrogen peroxide to molecular oxygen and water (Schoonen et al., 2010). Hence, the expectation is that in a galvanically coupled system there will be a higher net generation rate of hydroxyl radical via the Fenton reaction than in an uncoupled system because loss of hydrogen peroxide via decomposition to

water and molecular oxygen is limited. Alternatively, if the two metal sulfides are not galvanically coupled, both sulfides are expected to generate hydrogen peroxide and hydroxyl radicals independently. Hence, if there is no interaction between the two sulfides, it is expected that the rate of hydroxyl formation can be predicted on the basis of the rate of hydroxyl radical formation in dispersions of the endmembers. Thus, it is expected that studying the rate of hydroxyl radical formation in mixed systems will lead to a deeper insight into the level of galvanic coupling in mixed dispersions. These insights are of importance in understanding the potential health effects of co-exposures and the same insights may also be used to design new, more effective systems to degrade persistent organic molecules.

The conversion of the nucleobase adenine is used to evaluate the formation of hydroxyl radical in mixed pyrite-chalcopyrite dispersions. Adenine is oxidized by mineral-induced $\cdot\text{OH}$ radicals to 2-hydroxyadenine and 8-oxoadenine and can be used as a hydroxyl radical probe (Cohn et al., 2010). Adenine is stable in mineral-free, dilute hydrogen peroxide solutions and acid solutions (pH 1.8) as well as neutral solutions (Schoonen et al., 2010). While adenine decomposes in air-saturated pyrite slurries, it is stable in oxygen-free pyrite slurries and in air-saturated slurries with added ethanol or catalase. Ethanol scavenges $\cdot\text{OH}$, while catalase decomposes its precursor, H_2O_2 (Cohn et al., 2010; Schoonen et al., 2010). Hence, adenine is a suitable recorder molecule, or probe, of OH radical formation in the system of interest.

The $\cdot\text{OH}$ -mediated degradation of a variety of probe molecules in mineral dispersions has been used to determine the rate of OH radical formation (Fisher et al., 2012; Kwan and Voelker, 2003). The reaction between a probe molecule, here adenine (Aden), and $\cdot\text{OH}$ is a second order reaction dependent on the available mineral surface (Fisher et al., 2012). Hence, the decomposition rate of adenine can be expressed as follows:

$$\text{Rate} = d[\text{Aden}]/dt = -k_I A_s [\text{Aden}] [\cdot\text{OH}] \quad (7),$$

where A_s is the available metal sulfide surface area, k_I is the rate constant, and $[\text{Aden}]$ and $[\cdot\text{OH}]$ are the respective reactant concentrations. Earlier work (Kwan and Voelker, 2003; Pham et al., 2008; Tedder and Pohland, 2000) has shown that the conversion of the probe molecule often follows a pseudo-first-order rate law. This implies that the concentration of $[\cdot\text{OH}]$ has to be close to constant. Assuming a steady state concentration for hydroxyl radical ($[\cdot\text{OH}]_{ss}$), equation 7 can be simplified to:

$$\text{Rate} = d[\text{Aden}]/dt = -k^* A_s [\text{Aden}] \quad (8).$$

The reaction rate constant for the homogeneous reaction between adenine and $\cdot\text{OH}$ has been determined. The value of $k_{\text{OH-Aden}}$ is $6.1 \times 10^9 \text{ (mol}^{-1} \text{ sec}^{-1})$ (Steenken, 1989). Assuming that the reaction between $\cdot\text{OH}$ and adenine is rate determining then $[\cdot\text{OH}]_{ss}$ is equal to:

$$[\cdot\text{OH}]_{ss} = k^* A_s / k_{\text{OH-Aden}} \quad (9).$$

Hence, by determining k^* we gain insight into the steady-state concentration of $\cdot\text{OH}$. The intent of this study is to measure k^* as a function of pyrite/chalcopyrite surface ratio.

2. MATERIALS AND METHODS

Our hypothesis is that the addition of chalcopyrite to pyrite will increase the formation of $\cdot\text{OH}$ and increase the rate of adenine degradation. To test this hypothesis we conducted batch experiments in which we determined the loss of adenine over time as a function of chalcopyrite-to-pyrite ratio, solution pH, as well as in the presence of phosphate ions to impede electron transfer at the pyrite surface (Elsetinow et al., 2001). Each of these types of experiments and the materials used are described in detail in this section.

2.1. Materials

The pyrite and chalcopyrite used in the experiments were research-quality specimens from Huanzala, Peru, and Durango, Colorado, respectively. The minerals were first crushed with a hammer into mm-size grains and then pulverized in an agate ball mill (Retsch PM100). The samples were sieved to obtain a 60-to-90 μm size fraction for pyrite and a less-than-125 μm size fraction for chalcopyrite, respectively. The particles were then acid washed with 0.1N hydrochloric acid to free the surface from oxides (Bebie et al., 1998). The pyrite sample was washed with acid twice. After the second wash the specific surface area was 0.785 m^2/g . The specific surface area of chalcopyrite was 0.474 m^2/g . All specific surface areas were determined on a Quantachrom NOVA-2000 BET analyzer with UHP Nitrogen as adsorbate. An eight-point BET isotherm was collected and used to calculate specific surface areas. An IR spectrum was obtained for each of the materials to inspect the degree of surface oxidation before and after the acid washing. Diffuse Reflectance IR Fourier Transform spectroscopy was used to obtain the IR spectra. About ten mg of the material was mixed with dry KBr and the measurement was conducted on a Nicolet NEXUS 670 FTIR spectrometer equipped with a DGTS detector.

2.2. Adenine Batch Experiments

Adenine experiments were conducted in air-saturated solutions in polystyrene Falcon tubes at room temperature and followed the strategy used in earlier work (Cohn et al., 2010; Schoonen et al., 2010). Five sets of batch experiments were conducted in total, along with a set of control experiments to evaluate of the extent of adenine sorption on to pyrite in the absence of dissolved oxygen. Hence, the control experiments were conducted in anaerobic slurries, which eliminates the driving force for the production of hydroxyl radical. Three sets of experiments were conducted to determine the rate of adenine conversion in pure pyrite, pure chalcopyrite, and

mixed pyrite-chalcopyrite dispersions as function of solution composition. One of these three sets of experiments was conducted in deionized water (near-neutral starting pH; Experiments A), one in 0.02 N HCl (pH 1.8; Experiments B), and a third set in 0.01M phosphate buffer (pH 7.4; Experiments C). In a fourth set of experiments, the adenine conversion in pure pyrite, pure chalcopyrite, and mixed pyrite-chalcopyrite dispersions was determined as a function of total surface loading in deionized water (Experiments D). In the final set of experiments, the rate of adenine conversion was evaluated in mixed pyrite-chalcopyrite dispersions representing a range of pyrite-to-chalcopyrite surface area ratios, while the total surface area in the experiments was kept constant. This last set of batch experiments (E) as well as experiments D were conducted in deionized water. The conditions for each of the batch experiments are summarized in Table 1.

The initial adenine concentration was approximately 100 micromol/L in all the batch experiments. A 5mM adenine stock solution was prepared by dissolving adenine powder (Aldrich Chemicals) in UV-irradiated, ultra-filtered, deionized water (Easy Pure™ system, here after referred to as DI). The stock solution was stored in a standard refrigerator. A mineral-free blank experiment was included in each set of batch experiments. Throughout the course of the experiment adenine concentrations were determined on the basis of its absorbance at 260 nm. The absorbance measurements were conducted using a Hach DR/4000 UV-vis spectrometer with 1 cm quartz cuvettes. Dissolved metals, particularly iron, have a broad absorption band in the region of interest that leads to a sloping baseline (Cohn et al., 2010). To correct for this contribution to the absorbance signal, the solution was scanned from 230 to 290 nm so that the absorbance at 260 could be corrected for contributions from dissolved metals.

2.2.1. Anaerobic control experiments

Anaerobic control experiments were conducted with a pure pyrite dispersion, a pure chalcopyrite dispersion, and a 50-50 chalcopyrite-pyrite mixture. The experiments were conducted in 20ml glass septum vials. At the start of the experiment, 9.8ml DI (Easy Pure) was transferred into the septum vial by pipet and deaerated by passing a stream of N₂ through the solution for 15 minutes (Butler et al., 1994). After 15 minutes of purging, the N₂ gas stream was hooked up to a plastic funnel and placed over the vial to provide a N₂-rich headspace while allowing access for the addition of adenine and mineral powder. First, 200µl of a 5mM Adenine solution was added by pipet, followed by a known amount of solids to create slurries with a surface loading of 2.37 m²L⁻¹. The solids were weighed out on an analytical balance. The vial was tightly closed after adding the solids and agitated on a vibrator for 10 seconds. It was then covered with aluminum foil and incubated on an end-over-end rotator. One anaerobic blank experiment with only adenine was also included in this set of control experiments. To determine the concentration of adenine as a function of time samples were periodically withdrawn. To minimize exposure to air, the vial was opened under a funnel hooked up to a N₂ stream. A 1.5mL aliquot of the slurry was withdrawn into a 3mL airtight plastic syringe. A slip-on filter (0.45µm Millipore) was immediately attached to the syringe and filtrate was directly collected in a quartz cuvette for UV-vis analysis. The control experiments lasted for over 16 days.

2.2.2. Batch experiments A and B

Batch experiments A and B were conducted in 50mL polystyrene Falcon tubes. The appropriate amounts of metal sulfide were weighed out on an analytical balance and transferred into the tubes. In experiments A, 49 mL of DI was added along with 1mL of the adenine stock solution. In batch experiment A-3, 47 mL DI and 2 mL ethanol was added to an experiment with

chalcopyrite to determine if the conversion of adenine in the presence of chalcopyrite involves $\cdot\text{OH}$ as it does in the case with pyrite (Cohn et al., 2009). In experiments B, 49 mL of 0.02N HCl titrant (Fisher Scientific) was added along with 1 mL of the adenine stock solution. An experiment with ethanol and chalcopyrite was also included in batch experiments B (B-3). The tubes (experiments A and B), along with a particle-free control in each set of batch experiments, were wrapped in Al-foil to avoid photochemical reactions (Schoonen et al., 2000), vortexed for about 10 seconds to thoroughly mix the contents, and then placed on an end-over-end orbital shaker. Periodically, a 1.5 mL aliquot of sample was removed by syringe and filtered through a 0.45 μm Millipore slip-on filter into a quartz cuvette. The UV-spectrum for the sample was then collected immediately. The pH of each of the dispersions was measured using a combination electrode at the conclusion of the experiment.

2.2.3. Batch Experiments C, D, and E

Batch experiments C, D, and E were conducted in smaller, 15 mL Falcon polystyrene tubes, to minimize waste. After weighing out the appropriate amount of metal sulfide for Experiments C, 9.7 mL of deionized water along with 0.1 mL of 1M phosphate buffer and 0.2 mL of adenine stock solution were added, vortexed, wrapped in foil and placed on a orbital, end-over-end shaker. During the course of the experiments, the vials were temporarily removed from the orbital shaker and centrifuged at 2000 rpm for 25 minutes. About 1.5 mL of clear supernatant was then removed and the UV-absorbance was measured as described above. The solution was then returned to the tube and placed in the vortex mixer for about 10 seconds to disperse the metal sulfides, before they were placed back on the orbital shaker. Experiments D followed the same protocol, except that the total amount of metal sulfide was varied and no phosphate buffer was added. Experiments E were also conducted in deionized water without

phosphate, but the ratio of pyrite to chalcopyrite was varied, while the total surface area was kept constant.

3. RESULTS

For clarity the results of the anaerobic control experiments and batch experiments with adenine are presented separately.

3.1. Anaerobic Control Experiments

The results of the control experiments show that there is minimal adenine loss in pyrite dispersions under anaerobic conditions (Fig. 2a,b), consistent with earlier work (Cohn et al., 2010). The experiments with chalcopyrite-containing dispersions show a loss of about 20% of adenine within 24 hours followed by another 20% between 144 and 389 hours into the experiment (Fig. 2c and d). The change in adenine concentration based on the absorbance at 260 nm is shown in Figure 2f. The rate of loss of adenine in these control experiments was modeled using equation 8 (solid lines in Fig. 2f); the k^* values extracted from these model fits are summarized in Table 1.

3.2. Adenine Batch Experiments

The results for all five sets of batch experiments (A-E) to evaluate the formation of hydroxyl radical in aerated dispersions of pyrite, chalcopyrite, and pyrite-chalcopyrite mixtures are summarized in Table 1. It is important to note that in experiments A, B, and C, the 50/50 mixtures were created by adding the amounts of the endmembers used in the pure dispersions together. Thus the mixed dispersions in experiments A through C have a total surface area that equals the sum of the total surface area in each of the dispersions with the pure endmembers. In experiments D, the surface loading was varied to determine its influence on the reaction rate in

dispersions with the pure endmembers and a dispersion in which each endmembers contributed 50% of the total surface loading. For a given total surface loading, the value was the same regardless of the composition of the dispersion. In experiments E the influence of the composition of the dispersion was explored over a wide range of pyrite-to-chalcopyrite ratios, but all experiments were conducted with the same total surface loading. Hence, if the contributions of pyrite and chalcopyrite to the conversion of adenine is completely independent, the pseudo first order rate constant for the adenine conversion reaction (k^*) in mixed systems in Experiments A through C would be expected to be equal to the sum of the k^* values obtained in the dispersions with only the endmembers. By contrast, k^* values for mixed systems in experiments D and E are expected to be a linear combination of the k^* values obtained in pure endmember pyrite and chalcopyrite dispersions if the contributions of pyrite and chalcopyrite to the conversion of adenine are completely independent.

It is important to point out that the rate of adenine loss depends on the availability of oxygen, consistent with earlier work by Pham et al. (2008) on TCE degradation in pyrite slurries. The k^* values measured in aerated experiment A1, A2, and A4 are significantly higher than in the anaerobic control experiments with pyrite, chalcopyrite and the 50-50 mix (Table 1).

The results of the batch experiments show that the contributions of chalcopyrite and pyrite to the conversion of adenine are not independent in mixed dispersion, with the exception of experiments with phosphate. The data presented in Figure 3 are base-line corrected spectra for Experiments A (near-neutral starting pH). The stability of adenine in particle-free systems is illustrated with Fig. 3A. Adenine concentration decreases in the presence of chalcopyrite (Fig. 3B). There is a decrease of approximately 12% in concentration within the first 2 hours followed by a gradual decrease over time (Fig. 3B); however, addition of ethanol to a chalcopyrite

dispersion prevents this gradual adenine loss (Fig. 3C), but does not prevent the initial loss (13%). Addition of pyrite leads to loss of adenine (Fig. 3D) consistent with earlier results (Cohn et al., 2010; Schoonen et al., 2010), but the rate is significantly slower than for a dispersion with both pyrite and chalcopyrite present (Fig. 3E). Addition of ethanol to the mixed dispersion halts the adenine loss (Fig. 3F). As seen in the experiment with chalcopyrite, there is a decrease of 7% in adenine concentration within the first 2 hours in experiments with pyrite (Fig. 3D) and a 10 % drop in concentration in experiments with 50-50 mix with (Fig. 3E) or without ethanol (Fig. 2F). The base-line corrected absorbance values at 260 nm—the peak of adenine absorbance—are shown as a function of time for Experiments A, B, and C in Figure 4. The thin solid lines in Figure 4 are exponential fits through the data based on equation 8. The k^* values for these fits are summarized in Table 1 as well as the R^2 value for the linear regression of the natural logarithm of the adenine concentration plotted against time (i.e., linearizing equation 8 and obtaining k^* value from the slope of the line). Note that the k^* values for mixed systems in batch experiments A and B exceeds that of the sum of the pure endmembers by a factor of 4.86 and 6.27, respectively (see value of k^* _Ratio in Table 1). It is also clear that the addition of phosphate inactivates pyrite (Fig 4C). In the presence of phosphate, the decrease in adenine concentration for the mixed pyrite-chalcopyrite system equals that of the pure chalcopyrite system and the ratio of observed and expected rate based on a linear combination of the pure endmember (see value of k^* _Ratio, see Table 1) is below unity. Unlike pyrite, chalcopyrite reactivity appears to be unaffected by the addition of phosphate.

The reaction controlling the decrease in concentration of adenine is a surface-mediated process. The initial rates determined in batch experiments D based on the first 7 days of reaction show that the rate depends on the surface area loading (Fig. 5a), but the dependence is not

directly proportional (i.e., the slopes of the initial rate vs surface loading graph are close to two for the 50:50 pyrite-chalcopyrite experiments, while the slopes are less than unity for the experiments with the pure endmembers). The surface-normalized first-order rate constants for the mixed experiments show a dependence on surface area (Fig. 5b), whereas the rate constants for the experiments with the pure endmembers are independent of surface loading. The rate constants for the mixed experiments show a maximum at a surface loading of $2.37 \text{ m}^2/\text{L}$.

While experiments D include only one chalcopyrite-to-pyrite ratio, experiments E explore a range of chalcopyrite/pyrite ratios while the total surface area in the dispersion is kept constant at $4.71 \text{ m}^2/\text{L}$ (the highest loading in Experiments D). The results of batch experiments E indicate that pyrite-rich mixtures produce the most hydroxyl radicals on the basis on the adenine conversion rates. Figure 6 shows the baseline-corrected absorbances at 260 nm for each Experiment E in which the pyrite to chalcopyrite ratio was varied while the total surface area was kept constant. The solid lined through the data are a fit of the pseudo-first-order reaction rate law (eq. 8). It is evident, however, that this rate law does not match the measured data as well as a zero-order rate law (dashed line in Figure 6 panels A-F). The k^* for each of these fits based on the first-order rate law is plotted as a function of pyrite fraction in the mixture in Figure 7a. The k^* for the pure endmembers as well as a dashed line that represents the expected k^* values for mixed systems on the basis of a linear combination of k^* values for the two endmembers are also plotted in Figure 7a for comparison. The k^* values extracted from the experimental data is consistently higher than the calculated k^* values based on a linear combination of the endmembers. The maximum deviation is found for the 50-50 mix. Figure 7b shows the rate constant based on a zero-order rate law model (dashed lines in Figure 6). The rate constants for the zero-order model also show a deviation from the rate predicted based on a linear combination

of the rates of the two endmembers. However, for this model the maximum deviation is seen for the experiment with 90% pyrite in the dispersion. Table S1 provided a summary of the zero-order rate constant data for experiments E.

4. DISCUSSION

In all experiments with pyrite, chalcopyrite, and mixtures of pyrite and chalcopyrite there is a rapid initial loss of adenine followed with a gradual decrease in concentration, except for experiments with ethanol that show no further loss after the initial rapid decrease. Consistent with earlier work (Cohn et al., 2010; Pham et al., 2008), limiting the availability of dissolved molecular oxygen lowers the reaction rate significantly, but it does not prevent an initial rapid loss. Taken together, the control experiments in which the solution was purged (Table 1, X-series experiments) and the experiments with ethanol indicate (A-3 and B-3) that the initial rapid loss of adenine is not influenced by the presence or absence of oxygen or a radical scavenger. Hence, it is likely that sorption of adenine is responsible for the initial rapid loss, which is consistent with earlier work that showed that some adenine sorbs onto pyrite surfaces (Bebie and Schoonen, 2000; Sowerby et al., 2001). However, the gradual continued loss after this initial rapid loss requires the presence of oxygen and the absence of a radical scavenger. In earlier work on pure pyrite (Cohn et al., 2010), we have demonstrated that pyrite dispersed in aerated DI forms hydroxyl radicals that react with adenine to form 2-hydroxyadenine and 8-oxoadenine. That study also showed that either addition of ethanol to scavenge hydroxyl radical or catalase to decompose hydrogen peroxide stabilizes adenine. Hence, we infer from the data presented in Figure 3 that the mechanism for the gradual loss of adenine in pyrite, chalcopyrite, and mixed pyrite-chalcopyrite dispersions is driven by a reaction with $\cdot\text{OH}$, which is rate limiting. Hence,

the conversion of adenine is a proxy for $\cdot\text{OH}$ formation. Thus adenine conversion rates after the rapid initial loss provide insight into the rate of hydroxyl radical formation.

A comparison of the first-order model fits and zero-order model fits in Figure 6 and the linearity of the data presented in Figure 4b indicates that a zero-order model describes the data equally well or better than a first-order model (eq. 8) in many experiments. On the other hand, an experiment conducted as part of batch experiments D at a surface loading of $4.71 \text{ m}^2/\text{L}$ clearly shows that the loss of adenine in a 50:50 mixed dispersion follows a first-order rate law (Fig. 8). In the context of a surface-mediated process, a zero-order rate law indicates that a step at the surface is rate limiting followed by a rapid reaction with adenine regardless of its concentration. In that same context, a first-order rate law suggests that the rate-limiting step is the reaction between the radical and adenine. A further complication to consider is that with surface-mediated reactions a system may show a shift from first-order kinetics to zero-order kinetics as the concentration of the dissolved reactant (here adenine) increases for a given surface loading (Schoonen et al., 1998; Xu and Schoonen, 1995). OH radicals may only be produced on a small subset of surface sites, which may vary with pH or other conditions, such as presence of competing adsorbates. The principal objective of this study is to determine the rate of OH radical formation as function of the pyrite-to-chalcopyrite surface-loading ratio in the dispersion. Hence, for consistency, we are basing the discussion of the experimental data on a comparison of first-order rate constants. As explained below, the major conclusions are not dependent on this choice.

The adenine experiments show that hydroxyl radical formation in mixed pyrite-chalcopyrite systems is significantly faster than what would be expected on the basis of the two endmembers (Table 1 and Fig. 4). In fact, the k^* value in a mixed system with 40 to 60 % pyrite

(D-3, E-3, and E-4) is about a factor of two to three higher than expected on the basis of a linear combination of the rates measured for the endmembers (Fig 7a). The non-linearity holds for all batch experiments conducted here, except for the experiments with ethanol (A-3, B-3) and phosphate (experiments C). Applying a zero-order rate model supports the same conclusion (Fig 7b). The addition of ethanol scavenges hydroxyl radical as discussed above (Fig. 3, 4ab). The addition of phosphate is known to inhibit the transfer of electrons to oxygen at the pyrite surface (Elsetinow et al., 2001). The mixed system treated in phosphate buffer has an adenine conversion rate equal to that measured with chalcopyrite (Fig. 4), which indicates that in the presence of phosphate ions electron transfer reactions continue to occur at the chalcopyrite surface, but not on the pyrite surface.

The rate of adenine conversion appears to be slower in acid solutions. The adenine conversion in experiments at pH 1.8 is slower than those starting at near-neutral pH (Table 1 and Fig. 3). It is not clear what might cause this difference in rate. One possible explanation is based on the notion that the presence of Fe^{III} -(hydr)oxide patches facilitates electron transfer at pyrite and chalcopyrite surfaces (Elsetinow et al., 2001; Murphy and Strongin, 2009; Rosso et al., 1999; Usher et al., 2004). The presence and development of Fe^{III} -(hydr)oxide on pyrite surfaces at near-neutral pH has been confirmed by various spectroscopic techniques (Elsetinow et al., 2001; Murphy and Strongin, 2009; Rosso et al., 1999; Usher et al., 2004). Separate studies of oxidation products on chalcopyrite using Raman (Parker et al., 2008) and synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy (Goh et al., 2006) show the formation of elemental sulfur and iron hydroxide phases.

In acid solutions, a smaller area of the pyrite surface is expected to be covered by these patches as the solubility of Fe^{III} -(hydr)oxides increases with lower pH. So, on one hand the

patches are thought to facilitate the transfer of electrons from pyrite to molecular oxygen, but these same patches are likely also responsible for the decomposition of hydrogen peroxide to water and oxygen (Schoonen et al., 2010). Hence, it is possible that a low surface density of patches leads to a slow H_2O_2 formation rate, while a high surface density leads to a high H_2O_2 decomposition rate. Ultimately, it is the balance between these two reactions that determines how much hydrogen peroxide is available for the formation of $\cdot\text{OH}$. Far less is known about the stability and prevalence of Fe^{III} -(hydr)oxides on chalcopyrite as a function of pH. Nor is it clear whether they play the same critical role in electron transfer reactions. Further studies in which the composition of both the pyrite and chalcopyrite surfaces are studied are needed to resolve the pH dependence of the net rate of H_2O_2 formation

The change in adenine over time in acid conditions appears to follow a zero-order rate law rather than a first-order rate law (Fig.4b). This suggests that the rate at low pH conditions is independent of the adenine concentration and that the rate is only dictated by the rate of $\cdot\text{OH}$ formation. A lower number of sites suitable for electron transfer at higher acidity as suggested above may explain the apparent zero-order kinetics. In essence, with an increase in acidity the system may shift from an adenine-limited reaction rate around pH 5 to a surface-limited reaction rate at pH 1.8.

While acid conditions appear to slow down the adenine conversion rate, the non-linearity of the k^* values at pH 1.8 (Table 1, $k^*_{\text{Ratio}} = 2.10$ for B-4) was similar to that observed at higher pH values (k^*_{Ratio} between 1.51 and 3.14, Table 1, D and E). Hence, pH does not appear to be a significant factor in determining the non-linear response observed in mixed systems.

The rate of adenine conversion is dependent on total surface loading at near-neutral conditions, supporting the notion that surface-mediated reactions are rate limiting (Fig. 5a). However, the rate of adenine conversion is not directly proportional to the total surface area in the dispersion. This is reflected by the fact that the slopes of the lines presented in Figure 5a deviate from unity. This and the fact that the k^* values for the mixed dispersion slurries vary with surface loading suggest that the rates depend on the number of particles in the system. While the rate of adenine conversion and, by extension, the rate of $\cdot\text{OH}$ formation is surface-dependent, it should be pointed out that this does not necessarily mean that the conversion of adenine takes place on the surface. The conversion reaction may take place in solution with $\cdot\text{OH}$ derived from hydrogen peroxide reacting with dissolved ferrous iron (eq. 5), where the formation rate of hydrogen peroxide is surface dependent (Fig. 1). This notion is supported by our earlier work on the degradation of phenylalanine in pyrite slurries (Fisher et al., 2012). The degradation of phenylalanine via a reaction with $\cdot\text{OH}$ is proportional to the total pyrite surface area in the system, but modeling of the rate data suggest that it is the formation of hydrogen peroxide at that surface that is the rate-limiting step. Hydrogen peroxide then decomposes to $\cdot\text{OH}$ via a Fenton mechanism either on the surface or in solution and reacts fast with an organic molecule (phenylalanine in the study by Fisher and coworkers (2012) and adenine in this study).

4.1 Mechanism

We set out in this study to evaluate the hydroxyl radical formation as a function of pyrite-to-chalcopyrite surface-loading ratio. The results suggest that in phosphate-free systems there is a synergistic effect between pyrite and chalcopyrite that leads to a maximum in k^* values when the two materials are present at approximately equal surface loadings (Fig. 7a). On the basis of a zero-order rate model, the maximum deviation is seen for the most pyrite-rich dispersion (Fig. 7b). We consider two models to explain the non-linearity of the mixed systems compared to a

prediction of rates (zero-order model) or k^* values (first-order model) based on a linear combination of the rates or k^* values for the two endmember. The first model is referred to as the “co-factor” model, while the second one is the galvanic model. Each of these models is briefly described below.

The co-factor model is based on the premise that non-linear $\cdot\text{OH}$ formation rates can arise in a system when a network of synergistic reactions emerges. This model is schematically represented in Figure 9. The key to this model is that the rate of hydrogen peroxide formation on chalcopyrite surfaces is significantly faster than on pyrite surfaces, while the conversion of hydrogen peroxide to $\cdot\text{OH}$ is faster in the presence of pyrite than chalcopyrite. If this model is correct, we expect a higher hydrogen peroxide formation in pure chalcopyrite dispersions compared to pure pyrite dispersions. We tested this notion using a set of simple batch experiments in which we determined the formation of H_2O_2 using leuco-crystal violet as a probe, following the protocol developed by Cohn et al. (2005). A key aspect of this test is that the conversion of H_2O_2 to $\cdot\text{OH}$ via the Fenton reaction is arrested by adding EDTA. The results of this proof-of-concept test—summarized in Table 2—indicate that chalcopyrite indeed generates far more hydrogen peroxide than pyrite. However, the results also indicate that the amount of H_2O_2 generated in the pyrite-chalcopyrite dispersion is not a linear combination of the two endmembers. In fact, the amount of hydrogen peroxide formed in the 50/50 pyrite-chalcopyrite mixture is about a factor of 2 higher than expected on the basis of a linear combination of the endmembers (Table 3). Hence, the results do support the co-factor model, but this model alone cannot explain the non-linear formation rate of H_2O_2 , indicating that the Galvanic model also plays a role.

The Galvanic model is based on the notion that electrons can be transferred from chalcopyrite to pyrite while oxygen preferentially interacts with the pyrite surface (Figure 1). The non-linear $\cdot\text{OH}$ formation in this model arises from the fact that the pyrite surface remains pristine as chalcopyrite donates electrons and passes these onto pyrite. This prevents the buildup of oxidation products on the pyrite surface, such as: Fe(III)-OH patches, intermediate sulfur species and elemental sulfur. The Fe(III)-OH patches promote electron transfer but may also facilitate the decomposition of H_2O_2 (Schoonen et al., 2010), while the sulfur-containing patches inhibit electron transfer to molecular oxygen. Effectively, only the electron transfer reactions between molecular oxygen take place at the pyrite surface in a galvanically coupled system with chalcopyrite, while in the absence of chalcopyrite the pyrite surface also needs to accommodate electron transfer reactions between water and disulfide to form sulfate. The Galvanic effect hinges on the availability of both sulfides, which may explain why the non-linearity based on k^* values (Fig. 7a) is most pronounced when the two sulfides are present in about equal surface loadings. This maximizes the chance for contact between a chalcopyrite and pyrite particle. This notion is further supported by the fact that the surface-normalized k^* values for the 50-50 experiments with variable particle loading (Experiments D3, D6, and D9) drop off with total particle loading. By contrast, the surface-normalized k^* values for the pure endmembers do not show this particle-loading dependence. The results of the adenine experiments also indicate that electron transfer between dispersed chalcopyrite and pyrite is facile. In other words, the results indicate that a permanent physical contact is not necessary to establish a Galvanic couple, which is consistent with earlier work on the oxidation rate of chalcopyrite in chalcopyrite-pyrite dispersions (Koleini et al., 2010). The formation of $\cdot\text{OH}$ appears to be promoted by the rapid formation of H_2O_2 on the chalcopyrite surface, coupled with a Fenton-like reaction facilitated by

pyrite. Hence, this particular system may be best characterized as a hybrid co-factor/Galvanic system since both processes are necessary to explain the non-linear formation rates of $\cdot\text{OH}$ and H_2O_2 .

4.2. Implications

The non-linear formation rate of $\cdot\text{OH}$ has interesting implications and provides new opportunities. The results suggest a new approach to the design of remediation strategies based on pyrite-mediated Fenton chemistry. Prior work by Pham (Pham et al., 2008) showed that $\cdot\text{OH}$ derived via the interaction of pyrite with dissolved molecular oxygen degrades trichloroethylene (TCE), which is a persistent organic pollutant. We project that the addition of chalcopyrite will enhance the reaction rate in such a system significantly. In addition, there might be a possibility to couple degradation of persistent organic pollutants to the extraction of copper from low-concentration copper-pyrite mixtures without resorting to bioleaching, which is compromised by the presence of pyrite as a result of high concentrations of reactive oxygen species formation (Jones et al., 2013a; Jones et al., 2009, 2013b). Of course, the non-linearity of the mixed system presents a challenge to the common modeling approach that is based on treating the reaction rates of minerals completely independently with reaction rate constants derived from experiments with only pure endmembers.

Beyond the specific mineral system studied here, the results of this study indicate that dispersions composed of minerals or solids that represent a galvanic couple can behave as a coupled system despite the fact that the two components are not permanently physically bound as in the classic Galvanic system. This notion opens up the possibility of creating dispersions of semiconducting minerals and/or synthetic semiconductors that behave as galvanically coupled systems while maintaining high surface area to promote surface reactions with dissolved electron donors and acceptors. By tailoring the composition of the dispersion it might be possible to

optimize systems to promote specific electron transfer reactions. The pyrite-chalcopyrite system studied here might be unique in that it produces a significant amount of $\cdot\text{OH}$, which is a species that exhibits reactivity toward a broad spectrum of organic molecules, biomolecules, and macromolecules. The system studied here has high reactivity, but low specificity. By changing the endmembers of the dispersion and the solution composition it might be possible to create systems that have a lower reactivity, but higher specificity.

The non-linear formation of $\cdot\text{OH}$ in the mixed pyrite-chalcopyrite system may also have health implications and points to the need for further studies in which co-exposures are studied. It is well known that the formation of $\cdot\text{OH}$ is detrimental to mammalian cells (Dizdaroglu et al., 2002; Imlay, 2003; Schoonen et al., 2006) as this radical is the most reactive species in aqueous environments (Pryor, 1986) and reacts with little specificity. The results of this work suggests that pyrite-chalcopyrite co-exposures might be more harmful than the effects of exposure to the endmembers alone. Both pyrite and chalcopyrite have been shown to induce cell death and ROS upregulation in human lung epithelial cells (Harrington et al., 2011; Harrington et al., 2013) but mixtures have not been evaluated.

Acknowledgements—*This research is part of the senior author's Ph.D. thesis at Stony Brook University. The study benefitted from discussions with former group member Andrea Harrington, two reviews of an earlier version of the manuscript, and the review by the Ph.D. thesis committee. The concept of forming hydroxyl radical using a combination of semiconducting minerals with the intent to use it for degradation of organic contaminants has been disclosed as Stony Brook Technology Disclosure R-8542. Partial funding for this work was received from US Department of Energy-Office of Science Basic Energy Science.*

539

540 **REFERENCES:**

- 541 Bae, S., Kim, D. and Lee, W. (2013) Degradation of diclofenac by pyrite catalyzed Fenton
542 oxidation. *Applied Catalysis B-Environmental* 134, 93-102.
- 543 Bebie, J. and Schoonen, M.A.A. (2000) Pyrite surface interaction with selected organic aqueous
544 species under anoxic conditions. *Geochemical Transactions* 2000.
- 545 Bebie, J., Schoonen, M.A.A., Fuhrmann, M. and Strongin, D.R. (1998) Surface charge
546 development on transition metal sulfides: An electrokinetic study. *Geochimica Et*
547 *Cosmochimica Acta* 62, 633-642.
- 548 Berry, V.K., Murr, L.E. and Hiskey, J.B. (1978) Galvanic interaction between chalcopyrite and
549 pyrite during bacterial leaching of low-grade waste. *Hydrometallurgy* 3, 309-326.
- 550 Butler, I.B., Schoonen, M.A.A. and Rickard, D.F. (1994) Removal of dissolved oxygen from
551 water: a comparison of four common techniques. *Talanta* 41, 211-215.
- 552 Che, H., Bae, S. and Lee, W. (2011) Degradation of trichloroethylene by Fenton reaction in
553 pyrite suspension. *Journal of Hazardous Materials* 185, 1355-1361.
- 554 Cohn, C., Laffers, R., Simon, S., O'Riordan, T. and Schoonen, M. (2006a) Role of pyrite in
555 formation of hydroxyl radicals in coal: possible implications for human health. *Particle*
556 *and Fibre Toxicology* 3, 16.
- 557 Cohn, C., Mueller, S., Wimmer, E., Leifer, N., Greenbaum, S., Strongin, D. and Schoonen, M.
558 (2006b) Pyrite-induced hydroxyl radical formation and its effect on nucleic acids.
559 *Geochemical Transactions* 7.

560 Cohn, C.A., Borda, M.J. and Schoonen, M.A. (2004) RNA decomposition by pyrite-induced
561 radicals and possible role of lipids during the emergence of life. *Earth and Planetary*
562 *Science Letters* 225, 271-278.

563 Cohn, C.A., Fisher, S.C., Brownawell, B.J. and Schoonen, M.A.A. (2010) Adenine oxidation by
564 pyrite-generated hydroxyl radicals. *Geochemical Transactions* 11.

565 Cohn, C.A., Laffers, R. and Schoonen, M.A.A. (2006c) Using yeast RNA as a probe for
566 generation of hydroxyl radicals by earth materials. *Environmental Science & Technology*
567 40, 2838-2843.

568 Cohn, C.A., Pak, A., Strongin, D. and Schoonen, M.A. (2005) Quantifying hydrogen peroxide in
569 iron-containing solutions using leuco crystal violet. *Geochemical Transactions* 6, 47-51.

570 Cohn, C.A., Pedigo, C.E., Hylton, S.N., Simon, S.R. and Schoonen, M.A.A. (2009) Evaluating
571 the use of 3'-(p-Aminophenyl) fluorescein for determining the formation of highly
572 reactive oxygen species in particle suspensions. *Geochemical Transactions* 10.

573 de Brito Benetoli, L.O., Cadorin, B.M., Baldissarelli, V.Z., Geremias, R., de Souza, I.G. and
574 Debacher, N.A. (2012) Pyrite-enhanced methylene blue degradation in non-thermal
575 plasma water treatment reactor. *Journal of Hazardous Materials* 237, 55-62.

576 Dixon, D.G., Mayne, D.D. and Baxter, K.G. (2008) Galvanox - a novel galvanically assisted
577 atmospheric leaching technology for copper concentrates. *Canadian Metallurgical*
578 *Quarterly* 47, 327-336.

579 Dizdaroglu, M., Jaruga, P., Birincioglu, M. and Rodriguez, H. (2002) Free radical-induced
580 damage to DNA: mechanisms and measurement. *Free Radical Biology and Medicine* 32,
581 1102 - 1115.

582 Elsetinow, A.R., Schoonen, M.A.A. and Strongin, D.R. (2001) Aqueous Geochemical and
583 Surface Science Investigation of the Effect of Phosphate on Pyrite Oxidation.
584 Environmental Science and Technology 35, 2252-2257.

585 Feng, Y., Wu, D.-l. and Ma, L.-m. (2012) Treatment of Cationic Red X-GRL wastewater by
586 pyrite catalyzed Fenton-like reaction. China Environmental Science 32, 1011-1017.

587 Fisher, S.C., Schoonen, M.A.A. and Brownawell, B.J. (2012) Phenylalanine as a hydroxyl
588 radical-specific probe in pyrite slurries. Geochemical Transactions 13.

589 Friedlander, L.R., Puri, N., Schoonen, M.A.A. and Karzai, A.W. (2015) The effect of pyrite on
590 Escherichia coli in water: proof-of-concept for the elimination of waterborne bacteria by
591 reactive minerals. Journal of Water and Health 13, 42-53.

592 Fubini, B. and Fenoglio, I. (2007) Toxic potential of mineral dusts. Elements 3, 407-414.

593 Goh, S.W., Buckley, A.N., Lamb, R.N., Rosenberg, R.A. and Moran, D. (2006) The oxidation
594 states of copper and iron in mineral sulfides, and the oxides formed on initial exposure of
595 chalcopyrite and bornite to air. Geochimica Et Cosmochimica Acta 70, 2210-2228.

596 Harrington, A.D., Hylton, S.A. and Schoonen, M.A.A. (2011) Pyrite-driven Reactive Oxygen
597 Species Formation in Simulated Lung Fluid: Implications for Coal Workers'
598 Pneumoconiosis. . . Environmental Geochemistry and Health 34, 527-538.

599 Harrington, A.D., Tsirka, S.E. and Schoonen, M.A.A. (2013) Inflammatory stress response in
600 A549 cells as a result of exposure to coal: Evidence for the role of pyrite in coal workers'
601 pneumoconiosis pathogenesis. Chemosphere 93, 1216-1221.

602 Imlay, J.A. (2003) Pathways of oxidative damage. Annual Review of Microbiology 57, 395-418.

603 Jones, G.C., Becker, M., van Hille, R.P. and Harrison, S.T.L. (2013a) The effect of sulfide
 604 concentrate mineralogy and texture on Reactive Oxygen Species (ROS) generation.
 605 Applied Geochemistry 29, 199-213.

606 Jones, G.C., van Hille, R.P. and Harrison, S.T.L. (2009) Sulfide mineral induced stress as a
 607 limiting factor in tank bioleaching performance. Advanced Materials Research 71-73,
 608 365-368.

609 Jones, G.C., van Hille, R.P. and Harrison, S.T.L. (2013b) Reactive oxygen species generated in
 610 the presence of fine pyrite particles and its implication in thermophillic mineral
 611 bioleaching. Applied Microbiology and Biotechnology 97, 2735-2742.

612 Kolehini, S.M.J., Aghazadeh, V. and Sandstrom, A. (2011) Acidic sulphate leaching of
 613 chalcopryrite concentrates in presence of pyrite. Minerals Engineering 24, 381-386.

614 Kolehini, S.M.J., Jafarian, M., Abdollahy, M. and Aghazadeh, V. (2010) Galvanic Leaching of
 615 Chalcopryrite in Atmospheric Pressure and Sulfate Media: Kinetic and Surface Studies.
 616 Industrial & Engineering Chemistry Research 49, 5997-6002.

617 Kwan, W.P. and Voelker, B.M. (2003) Rates of hydroxyl radical generation and organic
 618 compound oxidation in mineral-catalyzed Fenton-like systems. Environmental Science &
 619 Technology 37, 1150-1158.

620 Majuste, D., Ciminelli, V.S.T., Osseo-Asare, K. and Dantas, M.S.S. (2012) Quantitative
 621 assessment of the effect of pyrite inclusions on chalcopryrite electrochemistry under
 622 oxidizing conditions. Hydrometallurgy 113, 167-176.

623 Matta, R., Hanna, K. and Chiron, S. (2007) Fenton-like oxidation of 2,4,6-trinitrotoluene using
 624 different iron minerals. Science of the Total Environment 385, 242-251.

625 Matta, R., Hanna, K., Kone, T. and Chiron, S. (2008) Oxidation of 2,4,6-trinitrotoluene in the
 626 presence of different iron-bearing minerals at neutral pH. *Chemical Engineering Journal*
 627 144, 453-458.

628 Mehta, A.P. and Murr, L.E. (1983) Fundamental studies of the contribution of galvanic
 629 interaction to acid-bacterial leaching of mixed metal sulfides. *Hydrometallurgy* 9, 235-
 630 256.

631 Murphy, R. and Strongin, D.R. (2009) Surface reactivity of pyrite and related sulfides. *Surface*
 632 *Science Reports* 64, 1-45.

633 Nazari, G., Dixon, D.G. and Dreisinger, D.B. (2011) Enhancing the kinetics of chalcopyrite
 634 leaching in the Galvanox (TM) process. *Hydrometallurgy* 105, 251-258.

635 Parker, G.K., Woods, R. and Hope, G.A. (2008) Raman investigation of chalcopyrite oxidation.
 636 *Colloids and Surfaces A: Physicochem. Eng. Aspects* 318 160–168.

637 Pham, H., Kitsuneduka, M., Hara, J., Suto, K. and Inoue, C. (2008) Trichloroethylene
 638 transformation by natural mineral pyrite: The deciding role of oxygen. *Environmental*
 639 *Science & Technology* 42, 7470-7475.

640 Plumlee, G.S. and Morman, S.A. (2011) Mine Wastes and Human Health. *Elements* 7, 399-404.

641 Pryor, W.A. (1986) Oxy-radicals and related species: their formation, lifetimes, and reactions.
 642 *Annual Review of Physiology* 48, 657-663.

643 Rosso, K.M., Becker, U. and Hochella, M.F. (1999) The interaction of pyrite {100} surfaces
 644 with O₂ and H₂O: Fundamental oxidation mechanisms. *American Mineralogist* 84, 1549-
 645 1561.

646 Schoonen, M.A.A., Cohn, C.A., Roemer, E., Laffers, R., Simon, S.R. and O'Riordan, T. (2006)
 647 Mineral-induced formation of reactive oxygen species, in: Sahai, N., Schoonen, M.A.A.

648 (Eds.), *Medical Mineralogy and Geochemistry*. American Mineralogical Society, pp. 179-
 649 221.

650 Schoonen, M.A.A., Elsetinow, A., Borda, M. and Strongin, D.R. (2000) Effect of temperature
 651 and illumination on pyrite oxidation between pH 2 and 6. *Geochemical Transactions* 4.

652 Schoonen, M.A.A., Harrington, A.D., Laffers, R. and Strongin, D.R. (2010) Role of hydrogen
 653 peroxide and hydroxyl radical in pyrite oxidation by molecular oxygen. *Geochimica Et*
 654 *Cosmochimica Acta* 74, 4971-4987.

655 Schoonen, M.A.A. and Strongin, D.R. (2005) Catalysis of electron transfer reactions at mineral
 656 surfaces, in: Grassian, V. (Ed.), *Environmental Catalysis*. CRC Press, Boca Raton, Fl, pp.
 657 37-60.

658 Schoonen, M.A.A., Xu, Y. and Strongin, D.R. (1998) An introduction to geocatalysis. *Journal of*
 659 *Geochemical Exploration* 62, 201-215.

660 Silva, L.F.O., Oliveira, M.L.S., da Boit, K.M. and Finkelman, R.B. (2009) Characterization of
 661 Santa Catarina (Brazil) coal with respect to human health and environmental concerns.
 662 *Environmental Geochemistry and Health* 31, 475-485.

663 Silva, L.F.O., Wollenschlager, M. and Oliveira, M.L.S. (2011) A preliminary study of coal
 664 mining drainage and environmental health in the Santa Catarina region, Brazil.
 665 *Environmental Geochemistry and Health* 33, 55-65.

666 Sowerby, S.J., Cohn, C.A., Heckl, W.M. and Holm, N.G. (2001) Differential adsorption of
 667 nucleic acid bases: Relevance to the origin of life. *Proceedings of the National Academy*
 668 *of Sciences of the United States of America* 98, 820-822.

669 Steenken, S. (1989) Purine bases, nucleosides, and nucleotides: aqueous solution redox
 670 chemistry and transformation reactions of their radical cations and e- and OH adducts.
 671 Chemical Reviews 89, 503-520.

672 Tedder, D.W. and Pohland, F.G. (2000) Emerging technologies in hazardous waste management
 673 8. Springer, NY.

674 Usher, C.R., Cleveland, C.A., Strongin, D.R. and Schoonen, M.A. (2004) Origin of oxygen in
 675 sulfate during pyrite oxidation with water and dissolved oxygen: An in situ horizontal
 676 attenuated total reflectance infrared spectroscopy isotope study. Environmental Science &
 677 Technology 38, 5604-5606.

678 Usher, C.R., Paul, K.W., Narayansamy, J., Kubicki, J.D., Sparks, D.L., Schoonen, M.A.A. and
 679 Strongin, D.R. (2005) Mechanistic aspects of pyrite oxidation in an oxidizing gaseous
 680 environment: An in situ HATR-IR isotope study. Environmental Science & Technology
 681 39, 7576-7584.

682 Wang, W., Qu, Y., Yang, B., Liu, X. and Su, W. (2012) Lactate oxidation in pyrite suspension:
 683 A Fenton-like process in situ generating H₂O₂. Chemosphere 86, 376-382.

684 Williams, L.B. and Haydel, S.E. (2010) Evaluation of the medicinal use of clay minerals as
 685 antibacterial agents. International Geology Review 52, 745-770.

686 Williams, L.B., Metge, D.W., Eberl, D.D., Harvey, R.W., Turner, A.G., Prapaipong, P. and
 687 Poret-Peterson, A.T. (2011) What makes a natural clay antibacterial? Environmental
 688 Science & Technology 45, 3768-3773.

689 Wu, D., Feng, Y. and Ma, L. (2013) Oxidation of Azo Dyes by H₂O₂ in Presence of Natural
 690 Pyrite. Water Air and Soil Pollution 224.

691 Wu, D.L., Liu, Y.X., Zhang, Z.Y., Ma, L.M. and Zhang, Y.L. (2015) Pyrite-enhanced
692 degradation of chloramphenicol by low concentrations of H₂O₂. *Water Science and*
693 *Technology* 72, 180-186.

694 Xu, Y. and Schoonen, M.A.A. (1995) The stability of thiosulfate in the presence of pyrite in low-
695 temperature aqueous solutions. *Geochimica Cosmochimica Acta* 59, 4605-4622.

696 Xu, Y. and Schoonen, M.A.A. (2000) The absolute energy positions of conduction and valence
697 bands of selected semiconducting minerals. *American Mineralogist* 85, 543-556.

698 Zhang, Y.Q., Tran, H.P., Hussain, I., Zhong, Y.Q. and Huang, S.B. (2015) Degradation of p-
699 chloroaniline by pyrite in aqueous solutions. *Chemical Engineering Journal* 279, 396-401.

700

701

702

703 Figure 1. Schematic diagram of galvanic pyrite-chalcopyrite system and the formation of hydroxyl radical, $^{\bullet}OH$, at the pyrite surface. Figure adapted from Schoonen et al. (2010), see text for details.

Figure 2. Base-line corrected adenine UV-absorbance spectra for anaerobic control experiments with adenine only (A) pyrite dispersion (B), chalcopyrite dispersion (C), and 50-50 mix pyrite-chalcopyrite (D) dispersion as well as a particle free adenine solution at four different time points, see Table 1 for experimental details. Panel E shows Absorbance at 260 nm as a function of time. Thin solid lines are first-order model fits to data.

712
713

Figure 3. Base-line corrected adenine UV-absorbance spectra for Experiments A, see Table 1. Panel A, particle-free adenine solution (100 micromol/L); B, chalcopyrite; C: chalcopyrite and ethanol; D: pyrite; E: Chalcopyrite and pyrite; F: Chalcopyrite and pyrite and ethanol.

Figure 4. Batch adenine conversion experiments A (top panel), B (middle), and C (bottom). Thin solid lines are model fits using first-order reaction rate law. See Table 1 for experimental details.

Figure 5. Dependence of initial adenine decomposition rate on surface loading.

Figure 6. Adenine conversion experiments as a function of pyrite-to-chalcopyrite ratio. In these experiments (experiments E in Table 1) the total surface area loading is constant and percentages refer to the fraction of the surface represented by pyrite and chalcopyrite (i.e., Cpy90Py10 is an experiment with 90% of the surface loading represented by chalcopyrite and the balance by pyrite). Solid lines are first order rate models (k^* value in Table 1), while dashed line is zero-order rate model (zero-order data summarized in supplemental Table S1).

Figure 7. Adenine conversion rate constants as a function of pyrite-to-chalcopyrite ratio. Panel A shows the first order rate constants for adenine degradation as a function of percentage of pyrite contributing to the surface loading in the experiment. Panel B shows zero order rate constants as a functions of percentage of pyrite contributing to the surface loading in the experiment. Rate constants based on linear regression of experimental data shown in Fig. 6 as a function of pyrite-to-chalcopyrite ratio. Note that the rate of conversion in mixed systems is significantly higher than expected on the basis of a linear combination of the rates of the two endmembers. Zero-order rate constant data available as supplemental materials, Table S1.

Figure 8. Adenine batch experiments D1, D2, D3, see Table 1 for specifics. The thin solid lines through the data are first-order model fits (eq. 8). The dashed line is a prediction of the adenine degradation rate based on a linear combination of the k^* values obtained for the endmembers. Note that the rate of adenine loss is significantly higher in the 50:50 mix compared to the predicted rate.

Figure 9. Schematic diagram of the “co-factor” model to explain the non-linear OH radical formation rate in mixed pyrite-chalcopyrite dispersions.

Table 1. Summary of experimental conditions and measured rates in adenine decomposition batch experiments [#]															
Anaerobic Control Experiments (near neutral starting pH)															
Run	SA-Py	SA-Cpy	SA_ratio	SA_tot	pH_init	pH_end	[PO ₄]	Ethanol	<i>k</i> [*]	SE	R ²	n	At=0	<i>k</i> _Ratio ^{**}	
X-Adenine	0	0	n.a.	0	5.4		0	0	0	--	--	--	100		
X-Pyrite	2.37	0	n.a.	2.37	5.4		0	0	1.89E-3	4.44E-4	0.90	4	99.7		
X-Cpy	0	2.37	n.a.	2.37	5.4		0	0	6.75E-3	2.62E-4	0.99	4	79.3		
X-50-50	1.18	1.18	1	2.36	5.4		0	0	6.88E-3	7.45E-4	0.98	4	83.8	1.59	
Experiment A. (near-neutral starting pH)															
Run	SA-Py	SA-Cpy	SA_ratio	SA_tot	pH_init	pH_end	[PO ₄]	Ethanol	<i>k</i> [*]	SE	R ²	n	At=0	<i>k</i> _Ratio ^{**}	
A-0	0	0	--	0	5.4		n.a.	0	2.40E-4	3.80E-4	0.03	7	99.9		
A-1	2.37	0	n.a.	2.37	5.4	3.73	n.a.	0	1.26E-2	4.98E-4	0.99	7	92.5		
A-2	0	2.37	n.a.	2.37	5.4	4.16	n.a.	0	1.09E-2	9.34E-4	0.97	7	85.3		
A-3	0	2.37	n.a.	2.37	5.4	4.17	n.a.	4	8.42E-4	3.01E-4	0.61	7	85.7		
A-4	2.37	2.37	1	4.74	5.4	4.11	n.a.	0	4.29E-2	8.49E-4	0.95	6	79.6	1.82	
Experiment B. (Acidic)															
Run	SA-Py	SA-Cpy	SA_ratio	SA_tot	pH_init	pH_end	[PO ₄]	Ethanol	<i>k</i> [*]	SE	R ²	n	At=0	<i>k</i> _Ratio ^{**}	
B-1	2.36	0	n.a.	2.36	1.8	1.97	n.a.	0	2.00E-4	1.86E-5	0.94	9	97.8		
B-2	0	2.37	n.a.	2.37	1.8	1.92	n.a.	0	2.70E-3	5.35E-5	0.99	9	94.9		
B-3	0	2.37	n.a.	2.37	1.8	2.2	n.a.	4	4.49E-4	6.11E-5	0.89	9	95.8		
B-4	2.36	2.37	1.00	4.73	1.8	2.7	n.a.	0	6.62E-3	8.67E-4	0.94	8	95.0	2.10	
Experiment C (Phosphate Buffer)															
Run	SA-Py	SA-Cpy	SA_ratio	SA_tot	pH_init	pH_end	[PO ₄]	Ethanol	<i>k</i> [*]	SE	R ²	n	At=0	<i>k</i> _Ratio ^{**}	
C-1	2.355	0	n.a.	2.36	7.4	7.4	10	0	8.69E-4	1.40E-4	0.81	11	93.3		
C-2	0	2.37	n.a.	2.37	7.4	7.4	10	0	6.50E-3	5.79E-4	0.93	11	79.6		
C-3	2.355	2.37	0.99	4.73	7.4	7.4	10	0	3.43E-3	2.01E-4	0.97	11	79.3	0.94	

Table 1. Continued														
Experiment D (Variable Surface Loading, <i>near-neutral starting pH</i>)														
Run	SA-Py	SA-Cpy	SA_ratio	SA_tot	pH_init	pH_end	[PO ₄]	Ethanol	<i>k</i> ^{###}	SE	R ²	n	At=0	<i>k</i> _Ratio ^{**}
D-1	4.74	0	n.a	4.74	n.d.	n.d.	n.a.	0	1.29E-2	2.58E-4	0.99	8	94.6	
D-2	0	4.71	n.a.	4.71	n.d.	n.d.	n.a.	0	9.87E-3	1.81E-4	0.99	8	78.0	
D-3	2.35	2.37	0.99	4.73	n.d.	n.d.	n.a.	0	4.18E-2	1.50E-3	0.99	6	84.8	2.72
D-4	2.35	0	n.a.	2.36	n.d.	n.d.	n.a.	0	1.12E-2	7.91E-5	0.99	10	95.5	
D-5	0	2.37	n.a.	2.37	n.d.	n.d.	n.a.	0	1.23E-2	2.04E-4	0.99	10	87.9	
D-6	1.18	1.19	0.99	2.36	n.d.	n.d.	n.a.	0	3.70E-2	9.25E-4	0.99	7	88.9	3.14
D-7	1.18	0	n.a.	1.18	n.d.	n.d.	n.a.	0	9.13E-3	4.04E-4	0.98	12	94.6	
D-8	0	1.19	n.a	1.19	n.d.	n.d.	n.a.	0	1.43E-2	1.35E-4	0.99	12	92.4	
D-9	0.59	0.59	0.99	1.18	n.d.	n.d.	n.a.	0	1.83E-2	4.84E-4	0.99	12	95.0	1.56
Experiment E (constant surface loading, variable Pyrite/Chalcopyrite ratio; <i>near-neutral starting pH</i>)														
Run	SA-Py	SA-Cpy	SA_ratio	SA_tot	pH_init	pH_end	[PO ₄]	Ethanol	<i>k</i> [*]	SE	R ²	n	At=0	<i>k</i> _Ratio ^{**}
E-1	0.47	4.27	0.11	4.74	n.d.	n.d.	n.a.	0	1.54E-2	7.17E-4	0.99	8	84.0	1.51
E-2	1.18	3.55	0.33	4.73	n.d.	n.d.	n.a.	0	2.43E-2	1.44E-3	0.98	8	88.9	2.29
E-3	1.89	2.84	0.66	4.73	n.d.	n.d.	n.a.	0	2.47E-2	1.14E-3	0.99	6	84.8	2.23
E-4	2.84	1.90	1.50	4.74	n.d.	n.d.	n.a.	0	2.91E-2	1.63E-3	0.99	6	89.9	2.49
E-5	3.55	1.18	3.00	4.73	n.d.	n.d.	n.a.	0	3.04E-2	2.28E-3	0.98	6	89.7	2.50
E-6	4.26	0.47	8.99	4.74	n.d.	n.d.	n.a.	0	2.54E-2	2.76E-3	0.96	6	97.3	2.03

#: In all experiments the starting adenine concentration was 100 micromole /L. SA, surface area in m²/L, SA_ratio is SA-Py/SA-Cpy; SA_tot is the total surface area available in experiment, calculated by adding SA_Py and SA_Cpy. Ethanol concentration in vol%, phosphate buffer concentration in micromole/L. SE is standard error in *k*^{*}, n is number of data points included in linear regression of lnAdenin-vs-time plot, At=0 is intercept of linear regression of lnAdenin-vs-time plot. ## Surface normalized first-order-rate constant (d⁻¹m⁻²). ***k*_Ratio is the measured rate constant (*k*^{*}) in mixed experiments divided by the calculated *k*^{*} based on a linear combination of surface area-weighted *k*^{*} values observed for the endmembers. A value of 1 indicates that the measured rate constant matches the calculated *k*^{*}. *k*_Ratio value in excess of 1 indicates that the system behaves non-linearly and leads to a higher decomposition rate than expected.

Table 2. Results leucocrystal experiments.

Experiment	Mineral Composition Dispersion		Catalase	H ₂ O ₂ (microM)
	Pyrite (mg)	Chalcopyrite (mg)		
X1	0	100	No	16.49
X2	0	100	Yes	0.24
X3	60		No	1.14
X4	30	50	No	20.58
Calculation*	30*	50*	No	10.86*

#All batch experiments where conducted with same total metal sulfide surface area loading. Solution volume of 13 mL, 1 mM EDTA. H₂O₂ recorded after 90 minutes of reaction time. In the mixed pyrite-chalcopyrite experiment (X4), 50% of the mineral surface area was pyrite, 50% chalcopyrite. Catalase was used in X2 to verify that purple color developed in X1 is due to H₂O₂. The addition of catalyse decomposes H₂O₂ before it can react with leucocrystal violet. This same type of control experiment was conducted by Cohn et al. (2005) in earlier work on pyrite dispersions. *Calculated value of H₂O₂ concentration for X4 based on linear combination of values obtained for X1 and X3.