



doi:10.1016/S0016-7037(02)01165-1

Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism

J. DONALD RIMSTIDT^{1,*} and DAVID J. VAUGHAN^{2,}¹Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA²Department of Earth Sciences and Williamson Research Centre for Molecular Environmental Science, University of Manchester, Manchester M13 9PL, UK

(Received October 29, 2001; accepted in revised form August 20, 2002)

Abstract—The oxidation of pyrite to release ferrous iron and sulfate ions to solution involves the transfer of seven electrons from each sulfur atom in the mineral to an aqueous oxidant. Because only one or, at most, two electrons can be transferred at a time, the overall oxidation process is quite complex. Furthermore, pyrite is a semiconductor, so the electrons are transferred from sulfur atoms at an anodic site, where oxygen atoms from water molecules attach to the sulfur atoms to form sulfoxy species, through the crystal to cathodic Fe(II) sites, where they are acquired by the oxidant species. The reaction at the cathodic sites is the rate-determining step for the overall process. This paper maps out the most important steps in this overall process. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

The oxidation of pyrite, the most abundant of all metal sulfide minerals, is the dominant process giving rise to the acidification of natural waters. Whether the source of the pyrite is shale or other rock with substantial accessory iron sulfide mineralogy, or dumps of waste material from a mining operation, the weathering of this pyrite can result in the acidification of large tracts of stream, river, and lake systems and the destruction of living organisms. Where anthropogenic influences have been involved, this is termed acid mine drainage (AMD), whereas the more general case is termed acid rock drainage (ARD). There is now a very substantial literature dealing with all aspects of AMD and ARD. Reviews and more general articles on this subject include those by Alpers and Blowes (1994), Banks et al. (1997), Evangelou (1995), Evangelou and Zhang (1995), Gray (1996), Jambor and Blowes (1994), (1998), Keith and Vaughan (2000), Nordstrom and Alpers (1999), and Salomons (1995).

In spite of many decades of research, the key controls of mechanisms and hence rates of the oxidation of pyrite remain poorly understood. This is largely because the processes of aqueous oxidation, which are relevant here, involve a complex series of elementary reactions. Basolo and Pearson (1967) pointed out that elementary steps of redox reactions almost always involve the transfer of only one electron at a time so that the oxidation of monosulfide minerals (e.g., sphalerite, galena) to release sulfate must require as many as eight elementary steps, and the oxidation of disulfides (e.g., pyrite and marcasite) must require up to seven elementary steps, depending on how elementary steps are defined. This process is further complicated by the fact that the minerals are semiconductors and the reactions are electrochemical in nature. This means that electrons can move from one part of the mineral to another so that the various reactions happen at different sites. Furthermore, the semiconducting properties of sulfide minerals such as pyrite are in turn critically dependant upon the precise composition of the

particular pyrite sample or even the zone or region of a particular sample. Thus, as further discussed below, subtle differences in stoichiometry influence electrical properties and may in turn significantly affect reactivity. This is certainly the case for electrochemical oxidation processes; however, the situation regarding chemical oxidation is less clear. As discussed below, there are differences in rates of oxidation for pyrite samples from different sources, although grain size (and hence surface area) differences may exert a greater control. Further studies are needed to resolve these issues.

The question that we wish to address in this article is how we can dissect the process of aqueous oxidation to reveal each of the elementary reaction steps and hence determine the key controls of reaction mechanisms and rates. Drawing upon our and our collaborators' research and upon other published material, we present our ideas in answer to this question in ways that have not previously been laid out in the literature. The emphasis here is on pyrite (FeS₂) oxidation, with some brief discussion of the oxidation of pyrrhotite (Fe_{1-x}S), as it is the iron sulfides that dominate natural systems. However, the principles developed below should apply to most, if not all, sulfide minerals.

2. REACTION MECHANISM

Pyrite oxidation is an electrochemical process that consists of three distinct steps, as illustrated in Figure 1. These three steps are the (1) cathodic reaction, (2) electron transport, and (3) anodic reaction. Each step will be discussed separately to simplify this presentation, but the steps must occur more or less simultaneously in the actual oxidation process.

2.1. Cathodic Reaction

The cathodic reaction involves an aqueous species that accepts electrons from an Fe(II) site on the mineral surface. There are many oxidants that can accept electrons from iron sulfide minerals, including NO³⁻, Cl₂, and H₂O₂, but the most important ones in nature are O₂ and Fe³⁺. These react with pyrite by the following overall reactions:

* Author to whom correspondence should be addressed (jdr02@vt.edu).

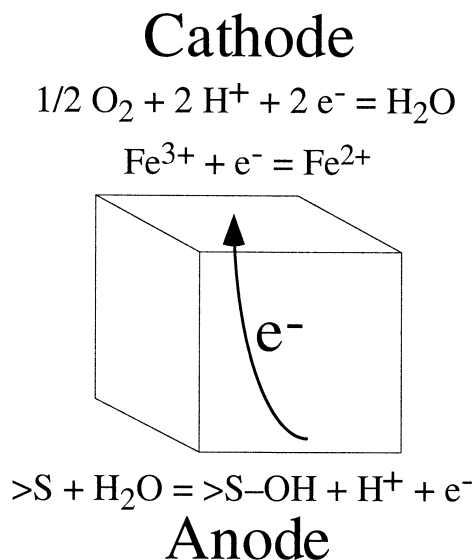
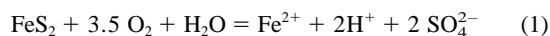
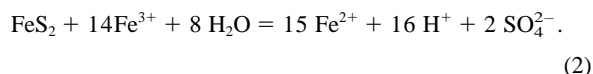


Fig. 1. The pyrite oxidation reaction consists of three steps. In the first step, a cathodic reaction transfers electrons from the surface of the pyrite to the aqueous oxidant species, usually O_2 or Fe^{3+} . The second step transports charge from the site of an anodic reaction to replace the electron lost from the cathodic site. In the third step, at an anodic site, the oxygen atom of a water molecule interacts with a sulfur atom to create a sulfoxy species. This releases an electron into the solid and one or two hydrogen ions to solution.



and



These balanced reactions show that the oxidation process does

not oxidize iron (it is Fe^{2+} in the mineral and remains Fe^{2+} as it is released into the solution), but rather, it oxidizes sulfur.

It is now clear that the cathodic reaction is the rate-determining step for sulfide mineral oxidation (e.g., Brown and Jurinak, 1989). Williamson and Rimstidt (1994) showed that the pyrite oxidation rate depends on the concentration of Fe^{3+} or O_2 (Figs. 2 and 3). Because the oxidant is involved in the activated complex, we can deduce that electron transfer from the sulfide to the oxidant, at the cathodic site, is the rate-determining step. Studies of the oxidation of galena, sphalerite, chalcocopyrite, and arsenopyrite (Rimstidt et al., 1994) show that this is also true for these minerals, and it is likely to be generally true. The exact nature of the cathodic site and the structure of the activated complex have not yet been documented, but there is evidence that electrons are transferred to the oxidant from metal sites in the mineral surface rather than from sulfur sites. For example, studies of the interaction of the pyrite {001} surface with O_2 and H_2O conducted under ultra-high vacuum conditions using scanning tunneling microscopy, along with ultraviolet photoelectron spectroscopy, support this view (Rosso et al., 1999). Surfaces exposed to O_2 show oxidative consumption of low-binding-energy electrons occupying dangling bond surface states localized on surface Fe atoms. When O_2 is combined with H_2O , there is a more aggressive oxidation of the surface, with discrete oxidation "patches" where reacted surface Fe sites have lost surface state density to the sorbed species. Thus, for pyrite, the activated complex might involve the transfer of an electron to a hydrated Fe^{3+} adsorbed from solution from Fe^{2+} in the mineral surface.



The Fe^{2+} is then released back to the solution, and an electron moves from an anodic site (described below) to reduce the Fe^{3+} back to Fe^{2+} . Likewise, Lowson (1982) proposed a Fenton-type mechanism for the reduction of O_2 at the surface of oxidizing pyrite. First, O_2 adsorbs at the Fe^{2+} site, and this

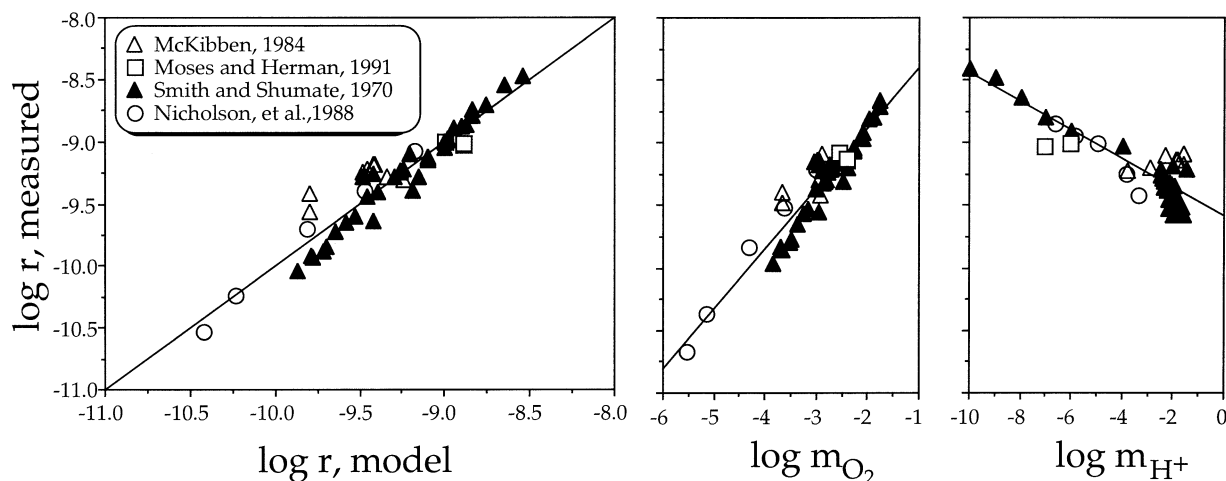


Fig. 2. Rate law for the oxidation rate of pyrite as a function of the concentration of O_2 and H^+ from Williamson and Rimstidt (1994). The equation that best fits these data, $r = 10^{-8.19} (m_{\text{O}_2}^{0.5} / m_{\text{H}^+}^{0.11})$, is similar to one derived from electrochemical experiments by Holmes and Crundwell (2000). This expression shows that the overall oxidation rate is proportional to the concentration of dissolved oxygen. This is consistent with the idea that the activated complex contains O_2 , which receives an electron from pyrite as the rate-determining step for the overall pyrite oxidation process.

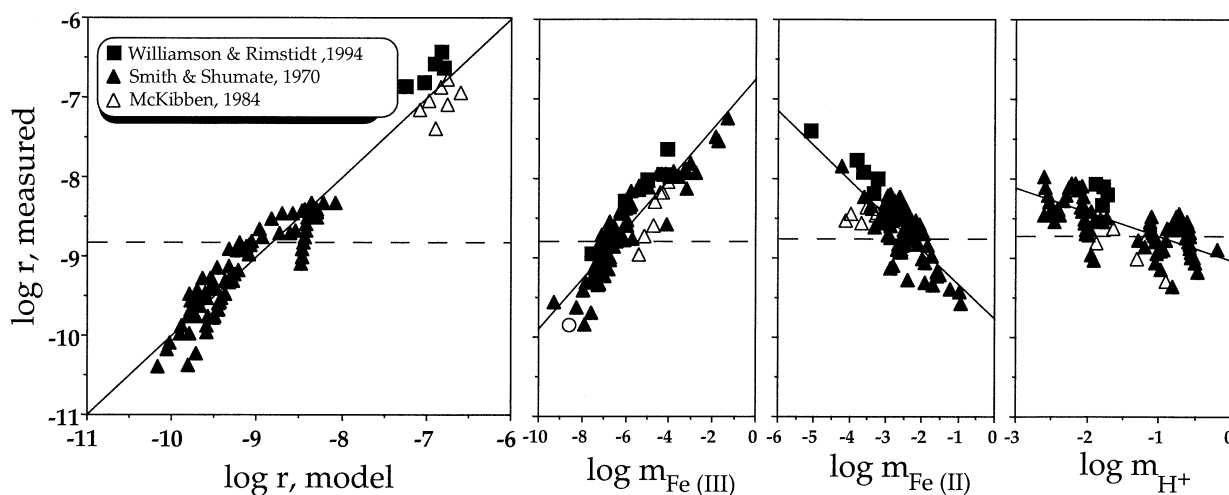
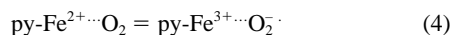
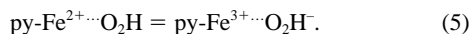


Fig. 3. Regression model for the oxidation rate of pyrite as a function of the concentration of dissolved Fe^{3+} and Fe^{2+} in oxygenated solutions from Williamson and Rimstidt (1994). The equation that best fits these data, $r = 10^{-6.07}(m_{\text{Fe}^{3+}}^{0.93}/m_{\text{Fe}^{2+}}^{0.40})$, is similar to one derived from electrochemical experiments by Holmes and Crundwell (2000). This expression shows that the rate is proportional to the concentration of Fe^{3+} , and this is consistent with the idea that the activated complex contains Fe^{3+} , which receives an electron from pyrite as the rate-determining step for the overall pyrite oxidation process.

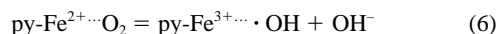
is followed by the transfer of an electron from this site to the O_2 :



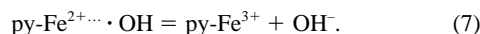
Then, a hydrogen ion reacts with the oxygen to produce HO_2 , and concurrently, an electron moves from an anodic site (described below) to reduce the Fe^{3+} back to Fe^{2+} . This allows another electron to be transferred to the oxygen.



An additional hydrogen reacts with this peroxide group to produce H_2O_2 , and concurrently, an electron moves from an anodic site (described below) to reduce the Fe^{3+} back to Fe^{2+} . The transfer of a third electron from the Fe^{2+} to the peroxide converts one of the oxygen atoms to a hydroxide ion that is released to the solution and the other to a $\cdot\text{OH}$ radical:



The Fe^{3+} is again recycled to Fe^{2+} by the transfer of another electron from the anodic site, and this electron moves to the $\cdot\text{OH}$ radical to convert it to OH^- , which is released to the solution:



Then, a final electron moves from an anodic site to reduce the Fe^{3+} back to Fe^{2+} , leaving the site the same as it was in the beginning of the process, even though four electrons were transferred through it.

2.2. Electron Transport

Clearly, the transport of electrons through the pyrite from the anodic site to the cathodic site from which they are transferred to the oxidant is a very important step in the oxidation process. Pyrite, like other sulfide minerals, is a semiconductor. The

conductivity of pyrites varies widely between 0.02 and 562 ($\Omega\text{ cm}$) $^{-1}$, with an average value of 48 ($\Omega\text{ cm}$) $^{-1}$ (Pridmore and Shvey, 1976; Doyle and Mirza, 1996). The conductivities of p-type pyrites are generally much lower than those of n-type samples, the mean conductivities being 0.5 and 56 ($\Omega\text{ cm}$) $^{-1}$ for p-type pyrites and n-type pyrites, respectively. Presumably, much of this variation in conductivity is related to the trace element composition. Pyrite exhibits considerable variability in terms of chemistry and electrical properties (Abraitis et al., 2003). Minor elements actually held within the lattice may include As (9.6 wt.%), Co (2.2 wt.%), Sb (0.7 wt.%), Au (0.3 wt.%), and Ni (0.2 wt.%), where the values in parentheses are the maximum reported values. Cu, Ag, and Sn may also occur as minor elements in the lattice but are typically present within mineral inclusions. Trace elements in pyrite include Ag, Bi, Cd, Hg, Mo, Pb, Pd, Pt, Ru, Sb, Se, Te, Tl, and Zn. Pyrite exhibits both n-type and p-type semiconducting behavior, and within a single pyrite specimen, there may exist zones exhibiting alternate n- and p-type behavior. Maps of typical trace element zoning in pyrite are shown in Craig et al. (1998). The S:Fe ratios of p-type pyrites are often > 2 . These materials also often contain significant quantities of As. The n-type pyrites may be sulfur deficient (i.e., have S:Fe ratios < 2) and may be relatively rich in Co and Ni.

Although there have often been claims of significant differences in the reactivity of pyrite and marcasite, the experimental evidence currently available does not bear them out. One of the few studies that has compared the reactivity of pyrite and marcasite from several sources (Wiersma and Rimstidt, 1984) showed that the most extreme difference between the rates of oxidation of pyrite and marcasite samples from several different sources was less than an order of magnitude and that the differences between most samples are approximately within the uncertainty of the rate measurements ($\sim\pm 50\%$) (see Fig. 4). The relatively good correlation between the rate data from experiments done in several different laboratories with several

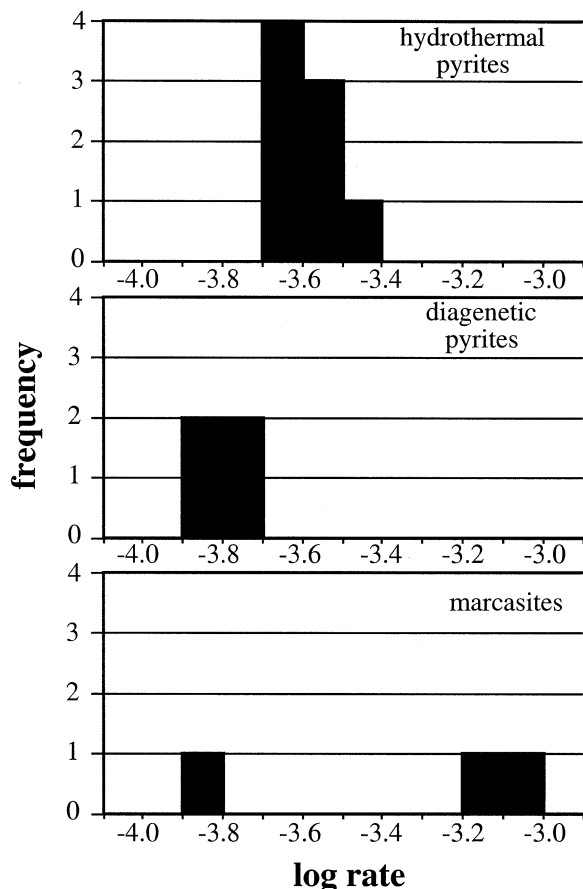


Fig. 4. Comparison of the rate of oxidation by ferric iron of pyrite and marcasite samples from various sources, showing that these rates do not vary systematically and differ by no more than ± 1 log unit. Data from Weirsmas and Rimstidt (1984).

different pyrite samples (Figs. 2 and 3) offers more evidence that pyrite and marcasite oxidation rates vary relatively little from sample to sample.

There are several ways to rationalize these results. First, we must consider that both pyrite and marcasite oxidation reactions are very far from equilibrium. The ΔG_r° for the oxidation of pyrite by oxygen as stated in Eq. (1) is -1180.8 kJ/mol (data from Robie and Hemmingway, 1995), but the difference in the free energy of formation of marcasite and pyrite is only 1.7 kJ/mol, or $\sim 0.14\%$ of this total. Thus, there is only a tiny difference between the chemical potential driving the oxidation of marcasite and pyrite so that any difference in their rates of oxidation would be best explained as either the result of variations in the reaction mechanism or the specific surface area, rather than the driving force for the overall reaction.

Our discussion of the cathodic reaction points out that the rate-determining step for sulfide mineral oxidation is the transfer of electrons from the mineral to the aqueous oxidant at the cathodic site. Rosso (2001), who provided an extensive review of the reactivity of semiconducting minerals, reported that the band gap of pyrite is 0.95 eV, whereas that of marcasite is 0.34 eV, so that there should be more electrons in the conduction band of marcasite, relative to pyrite, that would be available to transfer to the oxidant. Variation in the band gap of different

samples resulting from impurity contents may be sufficient to explain the relatively narrow range of observed oxidation rates within and among pyrite and marcasite samples. However, it is also possible that the trace element sites themselves participate as cathodic sites so that the number of cathodic sites varies as a function of trace element content. Together, these effects could easily account for the ~ 1 order of magnitude range of observed oxidation rates for pyrite and marcasite samples.

Still, there is no doubt that samples of pyrite and marcasite from different sources seem to deteriorate at much different rates during storage. Museum curators have long recognized that different samples of pyrite and marcasite display a wide range of reactivity (Howie, 1992). The best explanation for this observation available at this time was provided by Caruccio (1975), who pointed out that the one factor that seems to most affect the acid production rates for coal mine wastes is the size of the pyrite grains. Laboratory measurements have consistently shown that the oxidation rate is directly proportional to the exposed surface area. Therefore, it is not surprising that rocks that contain framboidal pyrite, which consists of micron- or submicron-sized crystals that have very high specific surface areas, produce acid at much higher rates than rocks containing larger sized pyrite or marcasite grains. Furthermore, when pyrite or marcasite oxidizes in moist air, salt weathering tends to fracture the crystals to increase the surface available for reaction. Salt weathering occurs because the molar volume of pyrite, 23.9 cm³, is much smaller than the molar volume of melanterite, 146.5 cm³ (Robie and Hemmingway, 1995), so when pyrite oxidation produces melanterite, or a similar hydrous iron sulfate salt, that crystallizes in the fractures and wedges the crystal apart, more and more surface area is created as the oxidation proceeds. This results in the well-known phenomenon of "pyrite disease," which destroys museum samples of pyrite and marcasite. Thus, it appears that variations in exposed surface area, which can be different by many orders of magnitude, are a much more important factor in controlling oxidation rate than composition or crystal structure, which seem to cause rate variations of < 1 order of magnitude.

2.3. Anodic Reaction

2.3.1. Oxidation Products

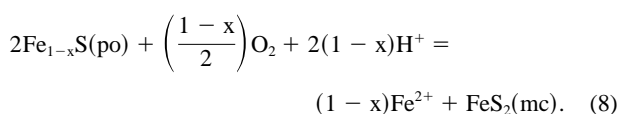
Sulfide mineral oxidation removes seven electrons from disulfide sulfur or eight electrons from sulfide sulfur to form sulfate. This means that the sulfur atoms must pass through several oxidation states during the oxidation process, so many different sulfur compounds might be involved. Because of the importance of sulfur in technology and in the environment, there have been many studies of the oxidation of aqueous sulfur species (e.g., Bamford and Tipper, 1972; Braga and Connick, 1982; Golodets, 1983; Martin and Hill, 1987; Anderson et al., 1989; Viaravanmurthy and Zhou, 1995), and minor amounts of some of these aqueous species have been identified in laboratory experiments (e.g., Goldhaber, 1983; Moses et al., 1987). However, most evidence suggests that aqueous sulfur species other than sulfate are not present at significant concentrations in AMD where Fe^{3+} is the most important oxidant and the pH is low. If a significant amount of sulfur species other than sulfate were produced under AMD conditions, there would be two or

more reservoirs of sulfur species, each with a different sulfur isotope fraction factor, and each of the resulting species, including sulfate, would have a sulfur isotope ratio that differs from the original sulfide mineral(s). Most studies of the sulfur isotope systematics of AMD show that the sulfur isotope ratio of the sulfate closely matches the sulfur isotope ratio of the sulfides (see the review by Toran and Harris, 1989). This evidence suggests that sulfate is the predominant oxidation product. Although some thiosulfate was found in the experiments of Moses et al. (1987) and Goldhaber (1983), it would not persist in AMD solutions. The laboratory studies of Williamson and Rimstidt (1993) showed that thiosulfate quickly forms a highly colored, purple complex with ferric iron so that even relatively small amounts of thiosulfate are visible in solutions that contain ferric iron. This complex decomposes to form tetrathionate and ferrous iron. In acidic solutions that lack significant amounts of dissolved ferric iron, thiosulfate reacts to form sulfite and very long chain polythionates that precipitate from solution as yellowish-white colloids (Davis, 1958). These polythionates eventually decompose to elemental sulfur. Neither tetrathionate nor elemental sulfur is found in significant amounts in association with weathering pyrite, leading us to suggest that aqueous sulfur species other than sulfate are not important players in the AMD environments, but they might occur in higher pH situations.

2.3.2. The Multistep Sulfur Oxidation Process

Because so many electrons must be removed from each sulfur atom to oxidize it to sulfate, this oxidation process is by far the most complex and difficult to understand process in sulfide mineral oxidation. Because it is unlikely that more than one electron is removed from the sulfur atom at a time (Basolo and Pearson, 1967), there must be several steps to this overall process. Williamson and Rimstidt (1992) investigated the thermodynamic stability of the aqueous species that might be intermediates in this oxidation process and showed that there is no simple step-by-step path whereby this reaction can occur via aqueous intermediates (Fig. 5). This is an argument in favor of the idea that almost all of the sulfur remains on the mineral surface throughout the oxidation process.

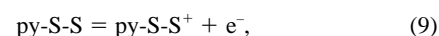
There is evidence that for many sulfide minerals, the first step in oxidation produces a sulfur-enriched surface, both on pyrite (Buckley and Woods, 1987) and on many other sulfide systems (see, e.g., Kartio et al., 1998). However, this is difficult to prove conclusively by experiment because sulfur, as a volatile species, is easily lost from the surface before analysis, particularly in standard ultrahigh vacuum surface analysis instruments. In the more extreme cases, this may involve the partial oxidation of sulfide sulfur to disulfide sulfur as in the oxidation of pyrrhotite (po) to form marcasite (mc) with ejection of Fe^{2+} into solution to maintain charge balance:



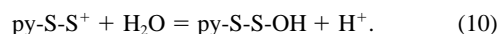
This type of "oxidative dissolution" reaction is common in sulfide minerals; for example, Goble (1981) showed that it is responsible for forming the so-called blaubleibender covellites

(now recognized as the minerals yarrowite and spionkopite). Oxidative dissolution always produces a mineral with a decreased cation content (increased sulfur content). Substantial cation loss from minerals can occur when the cations have high mobility in the mineral, as is the case for iron in pyrrhotite and copper in the copper and copper-iron sulfides. On the other hand, cation diffusion rates are low in most other sulfides (e.g., pyrite), so this process is more or less limited to the very near surface region, where it produces surface polysulfide groups, as identified by X-ray photoelectron spectroscopy studies (Buckley and Riley, 1991).

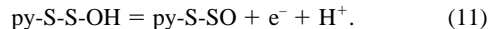
The key to understanding sulfide mineral oxidation involves following the oxidation of the sulfur atom. It seems that all of these reactions begin with disulfide (or perhaps larger polysulfide) groups that are produced by oxidative leaching. Further removal of electrons from the mineral at cathodic sites causes the terminal sulfur to become more electropositive.



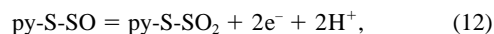
so that the negative end of the water dipole can mount a nucleophilic attack on this electropositive sulfur to produce a S-OH and release a hydrogen ion to solution.



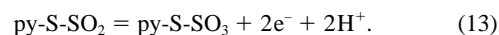
This hydrogen ion balances the positive charge lost from the solution at the cathodic site as an electron is transferred into the oxidant. The next electron removed from the mineral allows the S-S-OH group to release the second hydrogen to solution:



This cycle is repeated to produce py-S-SO₂, two more electrons, and two more hydrogen ions,



and then repeated again to produce py-S-SO₃, two more electrons, and two more hydrogen ions:



At this point, if the cation in the sulfide mineral is a relatively soft acid, there is a tendency for this species to break away from the surface as a thiosulfate complex:



The final step in the sulfur oxidation process appears to depend upon the pH. At high pH, the terminal S-SO₃ completely ionizes, making the S-S bond stronger than the Fe-S bond. As a result, much of the sulfur is released to solution as $\text{S}_2\text{O}_3^{2-}$. At low pH, the majority of the terminal S-SO₃ groups retain a proton, so they have the stoichiometry, S-SO₃H. This encourages the transfer of electrons into the S-S bond, where they are more easily transferred to the cationic site, leaving the terminal sulfur with a very positive charge. This leads to a fourth nucleophilic attack by a water molecule to produce SO_4^{2-} , which is released into the solution. Note that for cations that are soft bases, it is possible that an entire M-S-SO₃ moiety is released to the solution. Therefore, there appears to be a range of aqueous sulfur products ranging from almost 100% sulfate in

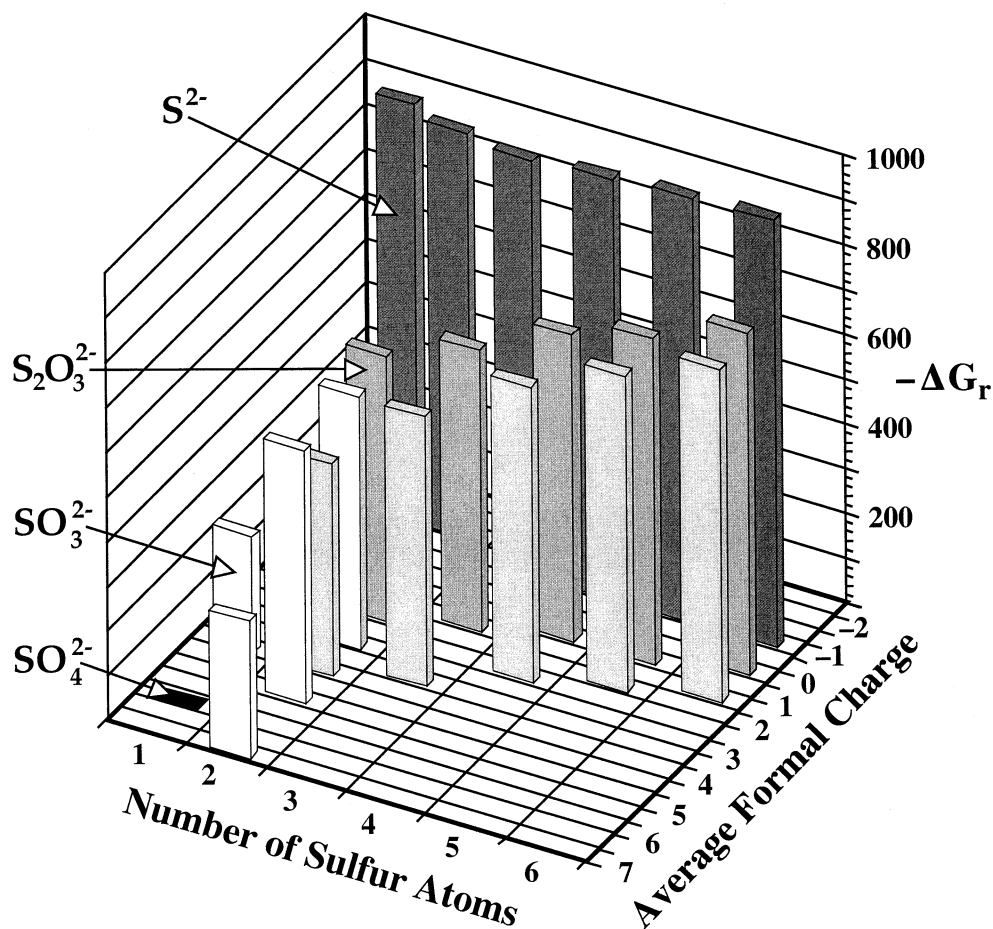


Fig. 5. ΔG_r° for the oxidation of aqueous sulfur species to form sulfate by the overall reaction $\frac{1}{x}\text{S}_x\text{O}_y^{2-} + \left(1 + \frac{1}{x}\right)\text{H}_2\text{O} + \left(\frac{3x - y + 1}{2x}\right)\text{O}_2 = \text{SO}_4^{2-} + \left(2 - \frac{2}{x}\right)\text{H}^+$. This diagram shows that there are significant gaps in the average formal charge on the sulfur atom between aqueous sulfur species with only one or two sulfur atoms. For example, oxidizing S_2^{2-} to $\text{S}_2\text{O}_3^{2-}$ would require the removal of three electrons per sulfur atom, an unlikely process given that there are no stable intermediate species. This suggests that most, if not all, of the oxidation steps involve surface sulfur species. Figure adapted from Williamson and Rimstidt (1992).

low-pH solutions to a fairly high proportion of thiosulfate and related products at higher pH.

Withdrawal of the last electron from the sulfoxy group to produces $\text{py-S-S}^+-\text{O}_3$ and one more water molecule reacts with the terminal sulfur to produce bisulfate:



This sequence of reactions consumes four water molecules and produces eight hydrogen ions per sulfur oxidized (see Eq. (2)) and accounts for the seven electrons that must be removed from each disulfide sulfur, S(-I), to produce sulfate sulfur, S(VI). This sequence of reactions is similar to that proposed in the context of Fe(III) oxidation by Moses and Herman (1991).

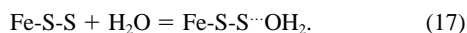
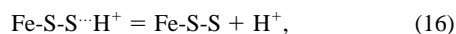
2.4. A Specific Case: Pyrite Oxidation in Acid (1 mol/L HCl) Solution

The reactions at the anodic sites are the most difficult to document both because they are quite complex and because

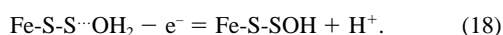
they cannot easily be studied using the standard kinetic methods for the rate-determining step. Instead, the nature of these reactions must be inferred by combining information from several sources. One of the most important of these is electrochemical study of pyrite oxidation.

The specific case of oxidation of pyrite in 1 mol/L HCl was discussed by Kelsall et al. (1999) in the light of electrochemical studies combined with spectroscopic investigations of the altered pyrite surface. This provides a useful example with which to develop the ideas presented above. The electrochemical data for the specific pyrite investigated showed very little reaction over a relatively wide range of potentials (between -0.4 and $+0.6$ V vs. S.C.E.). This was attributed to reversible adsorption/desorption of water and protons. Recalling that pyrite has a cubic crystal structure with Fe^{2+} ions at the corners and face centers of the cube unit cell and dumbbell shaped disulfide S_2^{2-} ions at the center of the cube and the midpoints of the cube edges, when pyrite is immersed in 1 mol/L HCl, H^+ ions can approach a Lewis base site S_2^{2-} and be adsorbed on it,

whereas the oxygen atom of water will be liable to approach a Lewis acid site Fe^{2+} and be adsorbed. However, as a positive potential is applied to the pyrite electrode, the electron cloud is pulled toward the bulk pyrite, leaving the positive end of a S_2^{2-} dipole exposed to the electrolyte. The adsorbed H^+ ions will be forced to desorb from the disulfide sites, and the oxygen atom of water will turn to these disulfide sites and be adsorbed here instead:



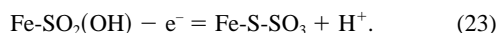
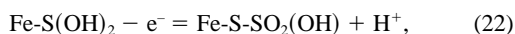
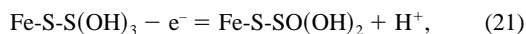
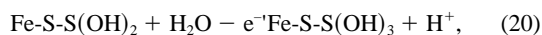
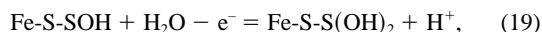
For the pyrite oxidation process to proceed, it is essential that oxygen atoms coordinate the sulfur atom. This occurs by a multistep process. As the electrode potential reaches further positive values, an electron in the Π^* antibonding orbital of S_2^{2-} will be extracted by the force of the external electrical field. Then, interaction between the Π^* antibonding orbital of S_2^{2-} the Π orbital of the water molecule will form a new bond, and a proton will be released:



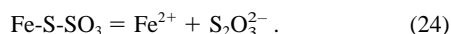
The main arguments for proposing that S_2^{2-} rather than Fe^{2+} loses an electron first may be stated as follows:

1. The nonbonding t_{2g} electrons in FeS_2 are localized and less reactive, whereas the antibonding Π^* electrons are delocalized and more reactive (see, e.g., the discussion in Tossell and Vaughan, 1992).
2. The ionization energy required to transform Fe^{2+} to Fe^{3+} is 2957 kJ mol^{-1} , much greater than that required to transform S to S^+ , 999 kJ mol^{-1} (National Bureau of Standards, 1970).
3. The standard Gibbs functions and experiment results indicate that Fe^{3+} ions can oxidize FeS_2 to S or SO_4^{2-} (see, e.g., reaction 2).

Therefore, under a positive applied potential, electrons in Π^* orbitals of S_2^{2-} would be lost first rather than those in t_{2g} orbitals of Fe^{2+} . Such electron transfer processes would continue if a positive external potential were applied to the pyrite, resulting in the following reactions:

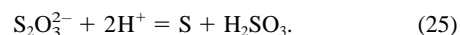


At this stage, it would be difficult to attach further water molecules to the sulfur atom and achieve electron transfer until the Fe-S or S-S bonds are broken. The Fe-S bond is relatively weaker than the S-S bond, so that the former would be broken to produce



On release into the electrolyte, six water molecules would octahedrally coordinate the Fe^{2+} ions. The ligand field imposed

by the six water molecules is weaker than that imposed by the six S_2^{2-} in pyrite so that the six 3d electrons of Fe^{2+} will change into a high-spin configuration. This will make the $\text{Fe}(\text{H}_2\text{O})^+$ easier to oxidize to Fe^{3+} than Fe^{2+} in pyrite because the latter is in a low-spin configuration. As is well known, $\text{S}_2\text{O}_3^{2-}$ is unstable in acidic solution (1 mol/L HCl) and will decompose very quickly to form



There are, however, uncertainties remaining regarding the importance of thiosulfate as a product, particularly when ferric iron is the oxidant, and this is another aspect of the oxidation of pyrite requiring further investigation.

3. CONCLUSIONS

The oxidation of pyrite is a complex electrochemical process requiring the transfer of seven electrons from each sulfur atom through the semiconducting crystal to an oxidant. This paper provides a brief summary of our attempt to create an internally consistent chemical and electrochemical model of the steps that must occur as pyrite oxidizes to form ferrous iron and sulfate ions.

Acknowledgments—J. Donald Rimstidt thanks the National Science Foundation for partial support of this research under grant EAR-0003364. David J. Vaughan thanks the Natural Environment Research Council and the Engineering and Physical Sciences Research Council for financial support and M. Farquhar, G. Kelsall, R. A. Wogelius, and Q. Yin for valuable discussions relating to ideas expressed in this paper.

Associate editor: G. Sposito

REFERENCES

- Abraitis P., Kendrick M., Patrick R. A. D., and Vaughan D. J. (in press) Variations in the compositional, textural and electrical properties of natural pyrite: a review. *Int. J. Miner. Process.*
- Alpers C. N., Blowes D. W. (1994) *Environmental Geochemistry of Sulfide Oxidation*. ACS Symp. Ser. 550. American Chemical Society, Washington, DC.
- Anderson L. G., Gates P. M., and Nold C. R. (1989) Mechanism of atmospheric oxidation of sulfur dioxide by hydroxyl radicals. In *Biogenic Sulfur in the Environment* (eds. E. S. Saltzman and W. J., 393 Cooper), pp. 437–449. American Chemical Society, Washington, DC.
- Bamford C. H. and Tipper C. F. H. (1972) Oxidation of sulfur compounds. In *Chemical Kinetics* (eds. C. H. Bamford and C. F. H., 6 Tipper), pp. 30–64. Elsevier, New York.
- Banks D., Younger P. L., Arnesen R.-T., Iversen E. R., and Banks S. B. (1997) Mine-water chemistry: The good, the bad and the ugly. *Environ. Geol.* **32**, 157–173.
- Basolo F., Pearson R. G. (1967) Oxidation-reduction reactions. In *Mechanisms of Inorganic Reactions: A Study of Metal Complexes in Solution*, pp. 454–525. John Wiley, New York.
- Braga T. G. and Connick R. E. (1982) Kinetics of the oxidation of bisulfite ion by oxygen. In *Flue Gas Desulfurization* (eds. J. L. Hudson and G. T. Rochelle), pp. 153–171. American Chemical Society, Washington, DC.
- Brown A. D. and Jurinak J. J. (1989) Mechanism of pyrite oxidation in aqueous mixtures. *J. Environ. Qual.* **18**, 545–550.
- Buckley A. N. and Woods R. (1987) The surface oxidation of pyrite. *Appl. Surf. Sci.* **27**, 437–452.
- Buckley A. N. and Riley K. W. (1991) Self-induced floatability of sulphide minerals: Examination of recent evidence for elemental sulphur as the hydrophobic entity. *Surf. Interface Anal.* **17**, 655–659.

- Caruccio F. T. (1975) Estimating the acid potential of coal mine refuse. In *The Ecology of Resource Degradation and Renewal, Vol. 15* (eds. M. J. Chadwick and G. T. Goodman), pp. 197–205. Blackwell, Oxford, UK.
- Craig J. R., Vokes F. M., and Solberg N. (1998) Pyrite: Physical and chemical textures. *Mineralium Deposita* **34**, 82–101.
- Davis R. E. (1958) Displacement reactions at the sulfur atom. I. An interpretation of the decomposition of acidified thiosulfate. *J. Am. Chem. Soc.* **80**, 3565–3569.
- Doyle F. M. and Mirza A. H. (1996) Electrochemical oxidation of pyrite samples with known composition and electrical properties. *Electrochem. Proc.* **96**, 203–214.
- Evangelou V. P. (1995) *Pyrite Oxidation and Its Control*. CRC Press, Boca Raton, FL.
- Evangelou V. P. and Zhang Y. L. (1995) A review: Pyrite oxidation mechanisms and acid mine drainage prevention. *Crit. Rev. Environ. Sci. Tech.* **25**, 141–199.
- Goble R. J. (1981) The leaching of copper from anilite and the production of a metastable copper sulfide structure. *Can. Mineral.* **19**, 583–591.
- Goldhaber M. B. (1983) Experimental study of metastable sulfur oxyanion formation during pyrite oxidation at pH 6–9 and 30°C. *Am. J. Sci.* **283**, 193–217.
- Golodets G. I. (1983) The oxidation of sulfur-containing inorganic compounds. In *Heterogeneous Catalytic Reactions Involving Molecular Oxygen* (ed. J. R. H. Ross), pp. 365–387. Elsevier, New York.
- Gray N. F. (1996) Field assessment of acid mine drainage contamination in surface and ground water. *Environ. Geol.* **27**, 358–361.
- Holmes P. R. and Crundwell F. K. (2000) The kinetics of the oxidation of pyrite by ferric ions and dissolved oxygen: An electrochemical study. *Geochem. Cosmochim. Acta* **64**, 263–274.
- Howie F. M. (1992) Pyrite and marcasite. In *Care and Conservation of Geological Material: Minerals, Rocks, Meteorites and Lunar Finds* (ed. F. M. Howie), pp. 70–84. Butterworths, Markham, Canada.
- Jambor J., Blowes D. W. (1994) *Environmental Geochemistry of Sulfide Minewastes*. Mineralogical Association of Canada Short Course 22.
- Jambor J. L., Blowes D. W. (1998) Theory and applications of mineralogy in environmental studies of sulfide bearing mine wastes. In *Modern Approaches to Ore and Environmental Mineralogy*. (eds. L. J. Cabri and D. J. Vaughan). Mineralogical Association of Canada Short Course 27.
- Kartio I. J., Laajalehto K., Suoinen E., Buckley E. J., and Woods R. (1998) The initial products of the anodic oxidation of galena in acidic solution and the influence of mineral stoichiometry. *Colloids Surf.* **A133**, 303.
- Keith C. N., Vaughan D. J. (2000) Mechanisms and rates of sulphide oxidation in relation to the problems of acid rock. (mine) drainage. In *Environmental Mineralogy: Microbial Interactions, Anthropogenic Influences, Contaminated Land and Waste Management*. Mineralogical Society Special Publication.
- Kelsall G. H., Yin Q., Vaughan D. J., England K. E. R., and Brandon N. P. (1999) Electrochemical oxidation of pyrite (FeS₂) in aqueous electrolytes. *J. Electroanal. Chem.* **471**, 116–125.
- Lowson R. T. (1982) Aqueous pyrite oxidation by molecular oxygen. *Chem. Rev.* **82**(5), 461–497.
- Martin L. R. and Hill M. W. (1987) The iron catalyzed oxidation of sulfur: Reconciliation of the literature rates. *Atmos. Environ.* **21**, 1487–1490.
- McKibben M. A. (1984) *Kinetics of Aqueous Oxidation of Pyrite by Ferric Iron, Oxygen and Hydrogen Peroxide From pH 1–4 and 20–40°C*. Ph.D. thesis, The Pennsylvania State University.
- Moses C. O. and Herman J. S. (1991) Pyrite oxidation at circumneutral pH. *Geochim. Cosmochim. Acta* **55**, 471–482.
- Moses C. O., Nordstrom D. K., Herman J. S., and Mills A. L. (1987) Aqueous pyrite oxidation by dissolved oxygen and ferric iron. *Geochim. Cosmochim. Acta* **51**, 1561–1571.
- National Bureau of Standards. (1970) National Standard Reference Data Series No. 34, p. 2.
- Nicholson R. V., Gillham R. W., and Reardon E. J. (1988) Pyrite oxidation in carbonate buffered solution: I. Experimental kinetics. *Geochim. Cosmochim. Acta* **52**, 1077–1085.
- Nordstrom D. K. and Alpers C. N. (1999) Geochemistry of acid mine waters. In *The Environmental Geochemistry of Mineral Deposits* (eds. G. S. Plumlee and M. J. Logsdon), pp. 133–160. Society of Economic Geologists, Littleton, CO.
- Pridmore D. F. and Shuey R. T. (1976) The electrical resistivity of galena, pyrite, and chalcocopyrite. *Am. Mineral.* **61**, 248–259.
- Rimstidt J. D., Chermak J. A., and Gagen P. M. (1994) Rates of reaction of galena, sphalerite, chalcocopyrite, and arsenopyrite with Fe(III) in acidic solutions. In *Environmental Geochemistry of Sulfide Oxidation, ACS Symp. Ser. 550* (eds. C. N. Alpers and D. W. Blowes), pp. 1–13. American Chemical Society, Washington, DC.
- Robie R. A., Hemmingway B. S. (1995) *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar. (105 Pascals) Pressure and at Higher Temperatures*. U.S. Geological Survey Bulletin 2131.
- Rosso K. M. (2001) Structure and reactivity of semiconducting mineral surfaces: Convergence of molecular modeling and experiment. *Rev. Mineral. Geochem.* **42**, 199–271.
- Rosso K. M., Becker U., and Hochella M. F. Jr (1999) The interaction of pyrite {001} surfaces with O₂ and H₂O: Fundamental oxidation mechanisms. *Am. Mineral.* **84**, 1549–1561.
- Salomons W. (1995) Environmental impact of metals derived from mining activities: Processes, prediction, prevention. *J. Geochem. Explor.* **52**, 5–23.
- Smith E. E., Schumate K. S. (1970) *Sulfide to Sulfate Reaction Mechanism*. Fed. Water Qual. Admin. Water Poll. Control Res. Series Report #14010 FPS, 02/70.
- Toran L. and Harris R. (1989) Interpretation of sulfur and oxygen isotopes in biological and abiological sulfide oxidation. *Geochim. Cosmochim. Acta* **53**, 2341–2348.
- Tossell J. A. and Vaughan D. J. (1992) *Theoretical Geochemistry: Application of Quantum Mechanics in the Earth and Mineral Sciences*. Oxford University Press, New York.
- Viaravanmurthy M. and Zhou W. (1995) Characterization of a transient +2 sulfur oxidation state intermediate from the oxidation of aqueous sulfide. In *Geochemical Transformations of Sedimentary Sulfur* (eds. M. Viaravanmurthy, M. Schoonen, T. Eglinton, G. Luther, and B. Manowitz), pp. 280–292. American Chemical Society, Washington, DC.
- Wiersma C. L. and Rimstidt J. D. (1984) Rates of reaction of pyrite and marcasite with ferric iron at pH 2. *Geochim. Cosmochim. Acta* **48**, 85–92.
- Williamson M. A. and Rimstidt J. D. (1992) Correlation between structure and thermodynamic properties of aqueous sulfur species. *Geochim. Cosmochim. Acta* **56**, 3867–3880.
- Williamson M. A. and Rimstidt J. D. (1993) The rate of decomposition of the ferric-thiosulfate complex in acidic aqueous solutions. *Geochim. Cosmochim. Acta* **57**, 3555–3561.
- Williamson M. A. and Rimstidt J. D. (1994) The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochim. Cosmochim. Acta* **58**, 5443–5454.