

Comment

Comment on “Pyrite dissolution in acidic media” by M. Descostes,
P. Vitorge, and C. BeaucaireGregory Druschel^{a,*}, Michael Borda^b^a Department of Geology, University of Vermont, Burlington, VT 05405, USA^b Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19716, USA

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2. Thiosulfate ($\text{S}_2\text{O}_3^{2-}$) release from pyrite surfaces**1. Introduction**

In a recent paper, Descostes et al. (2004) present data on a series of pyrite oxidation batch experiments conducted near pH 2 and 3 where they demonstrate very well the non-stoichiometric dissolution/oxidation of pyrite in acidic solutions through an extensive laboratory investigation of S/Fe ratios. The authors utilized this data to propose a ‘mechanism’ of pyrite oxidation based on these data. They conclude that measured sulfur deficiencies are due to a set of reactions involving thiosulfate ($\text{S}_2\text{O}_3^{2-}$) and tetrathionate ($\text{S}_4\text{O}_6^{2-}$) as the primary argument for presenting a specific pathway controlling pyrite oxidation. Using data taken from current literature, we challenge these assumptions regarding thiosulfate and tetrathionate reactivity and redefine these results in the context of a more complex, and more consistent, representation of pyrite oxidation pathways.

To avoid confusion concerning this discussion, we wish to clarify that while several points about the mechanism(s) (i.e., an elementary reaction described in its simplest, smallest increment) of specific steps have been presented, most of the points within this comment concern a description of the pathway(s) (i.e., an overall reaction that represents a number of steps) describing pyrite oxidation. Discrete definition of these terms may seem semantic; however, their proper use eliminates any potential misunderstanding of important intermediate steps which are necessary to ultimately understand the kinetics of the overall reaction under varying conditions. Herein, we will use the term pathway unless confident that the described reaction truly is an elementary reaction.

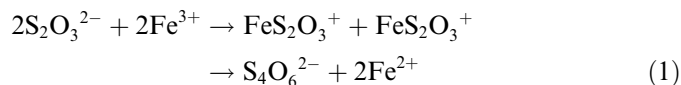
It is well accepted that thiosulfate is central in much of the thinking concerning pyrite oxidation pathways. Luther (1987) provided the theoretical framework supporting the role of thiosulfate as an initial soluble intermediate in the pathway of pyrite oxidation. Rimstidt and Vaughan (2003) also postulated a separate pathway for formation of thiosulfate on the surface of oxidizing pyrite. The difference between these two models, while an interesting and important matter concerning the mechanisms governing pyrite oxidation, is outside the scope of this comment and not necessarily addressed from the data presented in Descostes et al. (2004). Observation of thiosulfate and polythionates as a significant product of pyrite oxidation in solution has been restricted to more circumneutral pH (Goldhaber, 1983; Moses et al., 1987; Schippers et al., 1996; Schippers et al., 1999) while only low amounts of intermediate sulfur oxyanion species have been observed at lower pH (especially $\approx$ pH 2, a condition describing many acid mine drainage areas worldwide due to buffering by sulfate/bisulfate). The lack of observed soluble oxyanion species in several studies has been attributed in the past (Moses et al., 1987), and in (Descostes et al., 2004), to the rapid conversion of thiosulfate to tetrathionate and the subsequent rapid oxidation of tetrathionate to sulfate (SO_4^{2-}). Rimstidt and Vaughan (2003) specifically note the importance of uncertainties regarding thiosulfate as a product released from pyrite, in particular when ferric iron is the oxidant.

3. Fate of thiosulfate after release

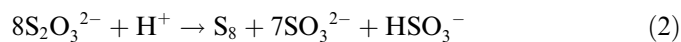
In waters containing ferric iron (Fe^{3+}), thiosulfate reacts to form tetrathionate via the following reaction:

* Corresponding author. Fax: +1 802 656 0045.

E-mail address: Gregory.Druschel@uvm.edu (G. Druschel).



(Williamson and Rimstidt, 1993). The reaction of thiosulfate to tetrathionate is also catalyzed by pyrite surfaces (Xu and Schoonen, 1995) and thiosulfate will disproportionate into elemental sulfur and sulfite (SO_3^{2-}) in acidic media:



(Johnston and McAmish, 1973; Xu and Schoonen, 1995). Competition between these processes (reactions 1 and 2) resulting in thiosulfate conversion to either elemental sulfur and sulfite, or tetrathionate, only becomes critical when the supply of ferric iron becomes limiting (Williamson and Rimstidt, 1993). While the fast decomposition kinetics for the FeS_2O_3^+ ions to tetrathionate are well defined by Williamson and Rimstidt (1993), they note that formation of the ferric thiosulfate complex is faster than they were able to measure and is thus likely several orders of magnitude faster than degradation of FeS_2O_3^+ . At pH 1.5, in the presence of excess ferric iron, thiosulfate conversion to tetrathionate is nearly complete, to the exclusion of elemental sulfur formation (Druschel et al., 2003). In any acidic solution containing an excess of ferric iron with respect to thiosulfate, we may reasonably expect polythionates as a predominant product, with any elemental sulfur formation being an indication that ferric iron has been primarily consumed. These reactions are easily observed in the laboratory as the FeS_2O_3^+ complex is bright purple, particulate elemental sulfur turns the solution milky white, and tetrathionate in solution is colorless.

4. Tetrathionate ($\text{S}_4\text{O}_6^{2-}$) reactivity

The next part of this pathway concerns the reactivity of tetrathionate under the conditions illustrated above. Druschel et al. (2003) documented the slow reaction kinetics of tetrathionate at pH 1.5 in the presence of O_2 and/or Fe^{3+} , and Motellier and Descostes (2001) document the slow oxidation kinetics of tetrathionate in lactic acid at pH 3.2. Given these results, if pyrite oxidation below pH 3 releases significant amounts of thiosulfate and the solutions contain excess ferric iron, then significant/measurable amounts of polythionates should be observed. Because the Descostes et al. (2004) experiments were run under these conditions (pH < 3 with measurable ferric iron), and the solutions were analyzed using a technique with low thiosulfate and tetrathionate detection limits (less than $5 \mu\text{M}$; Motellier et al., 1997; Motellier and Descostes, 2001), thiosulfate detachment as the intermediate defining the predominant pathway for these experiments should have resulted in significant polythionate concentrations.

5. Pyrite surface-bound thiosulfate

To address this seeming discrepancy concerning the mechanistic picture of pyrite oxidation towards the release

of thiosulfate, we turn to surface studies of pyrite oxidation at pH 2, monitored with attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy which indicate the formation of a surface-bound thiosulfate-like species on oxidizing pyrite (Borda et al., 2003b; Borda et al., 2004).

These results suggest that at low pH values (pH < 3) the pyrite oxidation pathway is controlled by a change in the Fe–S bond strength, retaining the thiosulfate-like moiety on the surface of pyrite and allowing subsequent reactions to break the S–S bond (Rimstidt and Vaughan, 2003). This change in strength of the Fe–S bond holding the thiosulfate-like moiety to the surface, instead of releasing it, is based on the above experimental evidence, and suggests a pH dependant change in the bond strength which is centered around pH 2, also near pK_2 for $\text{H}_2\text{S}_2\text{O}_3$ (Williamson and Rimstidt, 1992). The protonation of a surface-bound thiosulfate group draws electrons into the S–S bond (Rimstidt and Vaughan, 2003), which must add to the antibonding orbitals of the S–S moiety (Luther, 1987; Kelsall et al., 1999), weakening the bond.

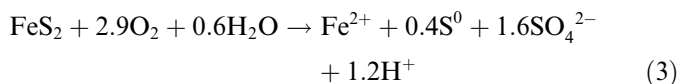
Borda et al. (2003b) suggest that the release species from the surface is sulfate, due to the infrared signature of a weakly bound (outer-sphere) sulfate species at the pyrite surface, however, spectral resolution could not rule out the possible existence of a sulfite-like species. Rimstidt and Vaughan (2003) discuss protonation of the surface thiosulfate-like group, where electron density is shifted to the S–S bond, creating a more electropositive terminal S which is open to nucleophilic attack by H_2O to form sulfate.

There is a striking consistency in the observation of thiosulfate, or a surface-bound species similar to thiosulfate, in a host of studies on pyrite oxidation. While, as we suggest below, there may be additional complexity in the pathways of pyrite oxidation, the molecular orbital arguments on pyrite oxidation started by Luther (1987) have withstood many tests. It is important to note that the lack of thiosulfate release into low pH solution observed in a number of pyrite oxidation experimental studies (McKibben and Barnes, 1986; Moses et al., 1987; Schippers et al., 1996; Descostes et al., 2004) is not an indication that the mechanism(s) to form surface bound $\text{S}_2\text{O}_3^{n-}$ is incorrect. Recent advances of both the surface species present under different conditions and the reactivities of bulk solution products facilitate this chance to refine our molecular picture of oxidizing pyrite.

6. Elemental sulfur formation during pyrite oxidation

The preceding arguments concerning thiosulfate and tetrathionate must also lead to a re-evaluation of the potential sources of elemental sulfur in these systems. The presence of elemental sulfur in significant amounts as a result of pyrite oxidation has been noted in other studies (Sasaki et al., 1995; Xu and Schoonen, 1995; Schippers et al., 1996; McGuire et al., 2001). Though Descostes et al. (2004) make no attempt to quantify experimentally the elemental sulfur

produced as a consequence of these reactions; they do impart a specific amount of elemental sulfur in their overall reaction for pyrite oxidation:



Their calculation of how much elemental sulfur must have formed is based on a mass balance calculation for a reaction where thiosulfate disproportionates into tetrathionate and elemental sulfur. No qualification, or experimental evidence, is provided for this reaction, except an argument based on a Pourbaix diagram, an argument in which the reaction progress trajectory was not considered. Their argument, based solely on thermodynamic relationships, is flawed for two reasons: (1) the conditions described for the reaction on this diagram indicate stability well outside of the ($\text{S}_2\text{O}_3^{2-}$) field, and even then a change towards the proposed disproportionation would require an Eh-pH change not supported by the experimental evidence; and (2) attempting to utilize a thermodynamic framework for these reactions is not appropriate, because the path dependence of a set of complex reactions would, by definition, be driven by kinetic considerations. All of the reactions discussed for thiosulfate and tetrathionate (plus many more, see (Xu and Schoonen, 1995)) are thermodynamically possible under the given conditions.

While Luther (1997) correctly argued that elemental sulfur can come from disproportionation of thiosulfate in acidic environments, there may additionally be an avenue of pyrite oxidation that is either independent of the thiosulfate-like surface species or a consequence of the fate of the thiosulfate-like surface species. If the surface-bound thiosulfate experiences bond breaking at the S–S bond, releasing a sulfite or sulfate molecule, the monosulfide left behind will undergo reactions at the surface or in solution after liberation. This scenario is likely closer to the reaction pathways governing oxidation of monosulfides such as galena and sphalerite, which are known to yield significant polysulfides and elemental sulfur in addition to sulfate products (Rimstidt et al., 1994; Schippers et al., 1996; Schippers and Sand, 1999; Weisener et al., 2003). This scenario may easily generate a $[\text{SO}_4^{2-}]/[\text{Fe}]_{\text{tot}}$ of less than 2, which would occur if all of the lone sulfide does not react with oxygen to form a sulfur oxyanion species. Numerous studies of monosulfide mineral oxidation indicate that while elemental sulfur is a product, much of the S is oxidized to sulfate. This process is a viable alternative to the $[\text{SO}_4^{2-}]/[\text{Fe}]_{\text{tot}}$ ratios that Descostes et al. (2004) attribute to thiosulfate disproportionation directly, but here we propose a separate pathway, similar to that described for pyrrhotite oxidation by Nicholson and Scharer (1994). Additionally, several electrochemical studies suggest that elemental formation may occur via a pathway that is independent of thiosulfate (Biegler and Swift, 1979; Holmes and Crundwell, 2000) and which likely involves an intermediate such as polysulfide

formation at the oxidizing pyrite surface (Flatt and Woods, 1995). This likely requires a S-enriched surface considering recent results on the inhibition of S polymerization by Fe on pyrite surfaces (Harmer and Nesbitt, 2004).

Schippers (2004) suggests a pathway for tetrathionate oxidation which may support the formation of elemental sulfur through disulfane-monosulfonic acid similar (but not identical) to the intermediates proposed by Druschel et al. (2003). However, experimental evidence from Druschel et al., (2003) does not support the formation of significant amounts of elemental sulfur from tetrathionate degradation under these conditions.

7. SO₂ loss

Descostes et al. (2004) suggest that there is a relationship between the amount of elemental sulfur and pH because the ratio $[\text{SO}_4^{2-}]/[\text{Fe}]_{\text{tot}}$ decreases with pH. Descostes et al. (2004) additionally suggest that this variation of $[\text{SO}_4^{2-}]/[\text{Fe}]_{\text{tot}}$ ratio may also/instead be due to SO₂ degassing. There is no experimental evidence for SO₂ degassing, and seemingly no attempt to calculate SO₂ degassing rates using established gas transfer kinetic theory. Sufficient fluxes of SO_{2(g)} can be calculated if one applies a simple two-film gas transfer model (as in Brezonik (1993)). However, the error associated with this calculation is on the order of the flux value required for development of the observed changes in $[\text{SO}_4^{2-}]/[\text{Fe}]_{\text{tot}}$. Without a correlation of $[\text{SO}_4^{2-}]/[\text{Fe}]_{\text{tot}}$ ratio with time, using this argument as a potentially critical aspect of pyrite oxidation pathways is tenuous. This hypothesis does illustrate the need for future studies to consider the role of SO_{2(g)} escape as a result of pyrite oxidation in different laboratory experiments and natural environments, as most acid mine drainage systems can, to some degree, be considered open.

8. Complex kinetic pathways for pyrite oxidation

Chemical reaction pathways are often complex and may exhibit sets of parallel, competing, inhibitory, back, and catalytic reaction steps; the basics of which are well described in texts on chemical kinetics (e.g., Brezonik, 1993). In any complex kinetic description, the rates of any step may be affected by different potential reactants in different ways, developing potential changes in pathways and selecting for wholly different paths based on the local geochemical environment. For a mineral, we also must take into account potential differences which may be due to changes in the bonding environments at the surface of different mineral faces (Guevremont et al., 1998; Rosso et al., 1999), and as the surface bonding environment changes as a function of step edges and corners (Becker et al., 2001). The rigidity of the model presented by Descostes et al. (2004) presumes to describe all of the reaction products as a consequence of one, and only one, set of sequential reactions, which must then be consistent over

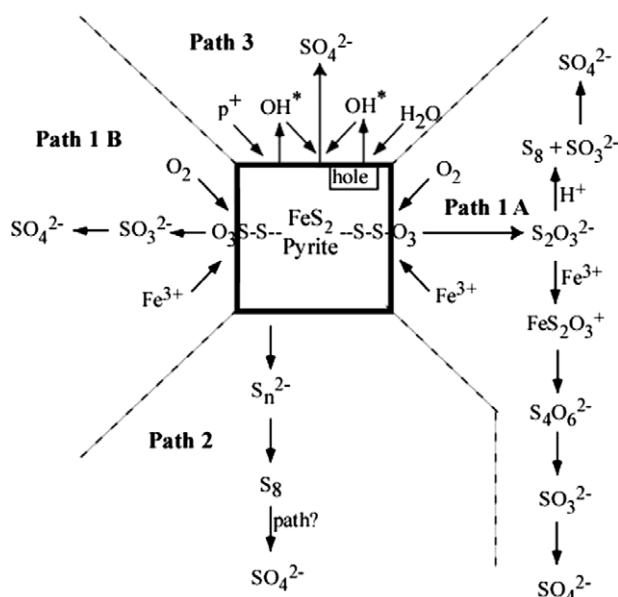


Fig. 1. Schematic representation of some of the possible reactions describing different pathways for pyrite oxidation. To the right is the thiosulfate pathway (Path 1A) where thiosulfate detaches and reacts, while to the left is the thiosulfate pathway where the Fe–S bond does not break; rather the S–S bond breaks, releasing sulfite which oxidizes to sulfate (Path 1B). To the bottom of the figure we represent the sulfide-polysulfide-elemental sulfur pathway (Path 2) and at the top is the defect/photochemically-driven pathway where holes or radicals react and drive S oxidation to sulfate (Path 3). Note that there are many more reactions which would fully describe these pathways than can be readily presented in one figure.

a range of conditions. It is the author's opinion that there is increasing evidence accumulated from the literature that pyrite oxidation may be viewed as a set of several different types of reaction paths (Fig. 1), generalized as the following:

1. The thiosulfate pathway: oxidation at the surface to form an Fe–SSO₃ surface structure, which may either detach as thiosulfate (Path 1A, Fig. 1) or as sulfite/sulfate (Path 1B, Fig. 1).
2. The sulfide-polysulfide-elemental sulfur pathway (Path 2, Fig. 1): while likely more prevalent in monosulfide minerals, the release of a sulfide or polysulfide may be related to path 1 or be independent, particularly as a function of how it is related to step-edge and corner features at the surface.
3. Defect/photochemically-driven pathway (Path 3, Fig. 1): either the presence of surface defects generating pseudo-holes (surface electron deficiencies), or photochemical electron-hole pair formation, can drive initial pyrite reactivity through interaction with surface waters (nucleophilic attack) and subsequent sulfur oxidation by OH* (Borda et al., 2001; Borda et al., 2003a; Druschel et al., 2004).

The reactivity of any of these intermediates may easily be affected by factors such as pH, temperature, availability

of different oxidants, reductants, ligands, or light in a way that will select for different pathways. The set of elementary reactions which comprise these mechanisms would be on the order of hundreds. Many of these reactions are affected by a host of surface, electrochemical (solid state and solution), photochemical, organic, and gas considerations not fully represented in this comment. We have documented a description of how the thiosulfate pathway is affected strongly, seemingly by pH, at a point in the pathway where the Fe–S bond strength is critical based on the results of Descostes et al. (2004) and other studies. It is the evaluation of these critical bifurcation points which will drive forward our understanding of sulfide mineral oxidation and the factors which affect it; however, a proper description of the *mechanistic* framework requires a kinetic description.

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