Oxidation of Sulfide Minerals: From Acid Mine Drainage to life on Mars

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Introduction
Pyrite, FeS₂, is the most abundant metal sulfide in nature and, therefore, has a major influence on the biogeochemical cycles of iron, sulfur, and oxygen. Oxidation of sulfide minerals near the Earth’s surface in the presence of water and oxygen frequently results in production of highly acidic, sulfate-rich solutions known as acid drainage. Acid drainage is commonly associated with the extraction and processing of sulfide-bearing metalliferous ore deposits, sulfide-rich coal, and weathering of metalliferous black shales.

Pyrite is the most widespread sulfide mineral on Earth forming in magmatic, metamorphic, or sedimentary settings. Pyrite-rich deposits are often mined for metals such as Cu, Zn, As, Pb, Hg, Au, and Ag, which are typically present as impurities in pyrite or occur in other sulfide minerals such as chalcopyrite (CuFeS₂), arsenopyrite (FeAsS), sphalerite (ZnS), and galena (PbS). The recovery of metals from sulfide-rich ore bodies is typically done by underground mining, strip mining, or open-pit mining. Mining, crushing to mineral recovery, followed typically by smelting of the sulfide ores results in production of large volume of sulfide-rich waste. Mine wastes are the largest volume of materials handled in the world. The oxidation of sulfide-rich waste exposed to air and water generate highly acidic toxic solutions (Fig. 1) that are referred to as acid mine drainage (AMD).

Mechanisms of abiotic pyrite oxidation
Oxidation of FeS₂ is an electrochemical process that involves concurrent stepwise cathodic and anodic reactions. Cathodic reactions engage aqueous species accepting electrons from Fe²⁺ on the pyrite surface. Anodic reactions involve stepwise oxidation of sulfur from S²⁻ disulfide in pyrite to S⁴⁺ in sulfate. The elementary steps of redox reactions involve the transfer of only one electron at a time, so that oxidation of disulfide to sulfate requires transfer of seven electrons and, hence, up to seven elementary steps (Rimstidt and Vaughan, 2003). The rate-limiting step is the electron transfer from pyrite to the oxidant at cathodic sites (Lefticariu et al., 2006a, Rimstidt and Vaughan, 2003). The oxidation of pyrite occurs when the mineral surface is exposed to an oxidant and water, either in oxygenated or anoxic systems. The main factors affecting the kinetics of pyrite oxidation are: the advection of oxidants (e.g., O₂, Fe³⁺, H₂O₂) to pyrite surfaces (Rosso et al., 1999, Rimstidt and Vaughan, 2003; Lefticariu et al., 2006a), temperature of reaction, solution chemical parameters (e.g., pH, Eh), and the presence or absence of microorganisms. In oxic surface environments on Earth, molecular oxygen (O₂) and ferric iron (Fe³⁺) are two dominant oxidants for pyrite.

Aqueous pyrite oxidation by O₂ is represented by the following overall reactions:
FeS₂ + 3.5O₂ + H₂O → Fe²⁺ + 2SO₄²⁻ + 2H⁺ (R1)
Ferrous iron (Fe$^{2+}$) is released into solution where it is oxidized by O$_2$ to ferric iron (Fe$^{3+}$):

$$4\text{Fe}^{2+} + O_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (R2)$$

Ferrous iron oxidation by O$_2$ at low pH is slow, thus the rate of the reaction in R2 may limit the rate of acid drainage generation. In fact, to create typical AMD, each packet of solution must be re-oxygenated many times along its flow path. The concentration of O$_2$ in groundwater is very small compared to the large requirement for O$_2$ in the reaction (R1). Therefore in suboxic and anoxic environments, pyrite oxidation critically depends on the presence of suitable oxidants. Thermodynamic considerations suggest that under anoxic conditions, ferric iron Fe$^{3+}$, manganese dioxide MnO$_2$ and nitrate NO$_3^-$ might oxidize pyrite (Schippers and Jørgensen, 2002). However, in abiogenic anoxic environments Fe$^{3+}$ is the only relevant oxidant of pyrite. Ferric iron (Fe$^{3+}$) is a powerful oxidant of pyrite in highly acidic conditions (Nordstrom and Alpers, 1999), and reacts with pyrite according to the following reaction:

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (R3)$$

This reaction results in the release of 16 mol of H$^+$ for each mole of pyrite oxidized.

Figure 2:
SEM microphotograph of iron sulfate minerals growing on pyrite surface during pyrite dissolution (Lefticariu et al., 2006a).

Analogous findings came from our previous work on abiotic pyrite oxidation by hydrogen peroxide (H$_2$O$_2$) at millimolar levels (Lefticariu et al., 2006a, 2007). Oxidation of pyrite by H$_2$O$_2$ produced supernatant solutions with low pH, high concentrations of SO$_4^{2-}$ and Fe$^{2+}$ and precipitates of iron sulfate minerals (Fig. 2). Microorganisms can catalyze sulfide oxidation, thus greatly increasing the rate of pyrite dissolution (Nordstrom and Alpers, 1999).

Biologically-mediated sulfide oxidation reactions

Recent studies have shown that microorganisms can survive and even thrive in environments that were previously thought voided of life, because they have finite nutrients and extreme living conditions. Such environments are associated with unusual physical or geochemically extreme conditions that are detrimental to the majority of life on Earth, such as extreme acidity, including very low or very high pH, extreme temperature, and high concentrations of sulfate and toxic metals. Bacteria are among the few forms of life that can tolerate these extreme environments. In acid drainage environments, eukaryotes (protists, fungi, and yeasts), archaea, and bacteria form a chemo-autotrophically-based biosphere largely responsible for the oxidation of sulfide minerals. Microbial activity can impact rates of sulfur oxidation during dissolution of pyrite, arsenopyrite, chalcopyrite, marcasite, and sphalerite (Blowes et al., 2007). The feedback between metabolic activity and mineral dissolution can drive the pH down to values <2, thus selecting for community members optimized for life in acid. DNA-based studies of organisms populating acid drainage environments have provided insights into the diversity of acidophilic, metal-tolerant species. Oxidation of sulfide ions to sulfate occurs via a series of intermediate sulfur-bearing compounds. Because protons are generated in the subset of reactions that add oxygen to the reduced sulfur species, microbial utilization of sulfide and intermediate sulfur compounds can significantly affect acidification, as well as pyrite dissolution rates. The genera Thiothrix, Acidithiobacillus, and Leptospirillum contain numerous species that can utilize various sulfur compounds as electron donor (Blowes et al., 2007). This group of organisms is largely responsible for the oxidation of sulfide minerals and includes iron- and sulfur-oxidizing bacteria.

One example of a recently studied acid mine drainage site is Tab Simco, which is an abandoned coal mine located southeast of Carbondale in Jackson County, Illinois (Lefticariu et al., 2009). The acid mine drainage discharges from the abandoned mine workings have low pH (~2.5) and high average concentration of dissolve ions: Fe = 597 mg/L, Al = 140 mg/L, Mn = 39.7 mg/L, and SO$_4^{2-}$ = 3,540 mg/L. To abate this problem a passive-type treatment system was constructed in 2007 by the Illinois Department of Natural Resources, Office of Mines and Minerals. The principle technology employed has been a 0.75-acre sulfate-reducing bioreactor, which is one of the first full scale system employed for the treatment of acidic, coal mine drainage in the US. The bioreactor was constructed in three layers: a shallow acid impoundment, an underlying thick layer of compost, and finally limestone with embedded drain pipes. A series of oxidation cells follow the bioreactor unit before discharge into Sycamore creek.
To analyze the bacterial community associated with the site, molecular analysis of DNA extracted from the acid mine pond, the bioreactor outlet, and the post-treatment pond was performed by amplification and cloning of the 16S rRNA gene (present in all bacteria) and the dissimilatory sulfite reductase genes (only found in sulfate-reducing bacteria). Preliminary results (Fig. 3) show that DNA sequences corresponding to bacteria capable of sulfate reduction were present (Lefticariu et al., 2009). However, the sequences were most similar to bacterial species that preferentially reduce nitrate over sulfate. This molecular data was supported by the subsequent isolation of Desulfovibrio strains capable of anaerobic sulfate reduction under controlled laboratory conditions. Sequences related to bacterial species that are not capable of sulfate reduction, but are able to use complex carbon sources such as cellulose were also detected.

While this finding is expected due to the presence of compost in the bioreactor, it suggests that simple dissolved organic carbon sources often utilized by sulfate reducers, such as lactate, may not be available to promote efficient bacterial sulfate reduction. Thus, the relatively high level of sulfate detected in the post-treatment pond is likely due to both the available organic substrate and the presence of nitrate. These results will be used to improve bioreactor design and ultimately the water quality at the AMD treatment site (Lefticariu et al., 2009).

Radiolytic oxidation of water coupled to oxidation of pyrite as a source of biosustaining energy

At depths greater than a few tens of meters below Earth's surface, aqueous fluids are often anoxic due to rapid utilization of oxygen and other electron acceptors by microbes in soil, sediment, and groundwater. In spite of presumed widespread anoxia, there is evidence of subsurface oxidation during the genesis of uranium roll-front deposits and the alteration of sulfide-bearing ores and coals (http://www.indiana.edu/~deeplife/). High concentrations of hydrogen and dissolved sulfate have been reported to sustain lithoautotrophic ecosystems in uranium-bearing crustal environments up to 2.8 kilometers below the surface of the Earth (Chivian et al., 2008). The geochemical origin of underlying energy and metabolic resources can be explained by radiolysis of water coupled to oxidation of sulfide minerals, such as pyrite (Lefticariu et al., 2006b, c, d). The process produces elemental hydrogen and partially to fully oxidized sulfur species in suitable proportions for maintenance and cell division of microbes (Chivian et al., 2008). Radiolytic dissociation of water produces a highly reactive combination of oxidizing (e.g., $H_2O^o$ and $H^-$ radicals) and reducing species (e.g., $H_2$) (Garrett et al., 2004, Pastina and Laverne, 2001). The radiolytic production of oxidants, including $H_2O$ and $H^-$ radicals, can turn an overall reducing environment into an oxidizing microenvironment, enhancing the weathering rate and raising the solubility of solid phases (Lin et al., 2006; Lefticariu et al., 2006d; Chivian et al., 2008). Oxidizing radicals are known to react rapidly and unselectively with many chemical species, extending to Fe and S sites on pyrite surfaces (Lefticariu et al., 2006d). The highly reactive species produced by -radiation of water (e.g., $H_2O^o$, $O_2^-$, and $H_2O^-$) can oxidatively accept electrons from Fe$^{3+}$ sites on the pyrite surface. Radiolytic oxidation of pyrite increases the level of complexity of the oxidation processes due to intricate interactions between radiation and liquid and solid media (Lefticariu et al., 2006d).

The following general reaction summarizes the radiolytic oxidation of pyrite at 25 °C:

$$ FeS_2 + 4 HO^o \rightarrow Fe^{3+} + S + SO_4^{2-} + 2H_2 $$

Radiolytic oxidation of pyrite is fundamentally controlled by the oxidation of reduced sulfur via two main processes: hydroxyl radical HO$^o$ and ferric iron Fe$^{3+}$ reduction pathways. The generation of these two chemical reagents is self-sustaining as long as radiolysis of water is continuing and regenerates reactive oxidizing species in the system (Lefticariu et al., 2006b). Recent studies have shown that radiolysis coupled to oxidation of sulfide minerals could produce gradients of both $H_2$ and sulfur species.
suitable for supporting microbial metabolism (Lin et al., 2006; Chivian et al., 2008). Bacterial oxidation of H₂ commonly occurs in nature (Pedersen et al., 2000). Highly diffusive H₂ is essential for life in environments where only trace amounts of organic carbon exist. In the deep subsurface, lithoautotrophic microbes can be fully independent of solar-driven photosynthesis by acquiring energy from the redox reactions involving H₂ with other electron acceptors (SO₄²⁻, Fe³⁺, or CO₂) to synthesize organic compounds. Radiolysis probably plays a hitherto unrecognized key role in lithotrophic / chemotrophic biological and geological subsurface weathering processes.

**Sulfates on Mars**

Recently, much interest has focused on sulfide oxidation due to the discovery of sulfate minerals on Mars and the similarity of Martian mineral assemblages with minerals associated with acid drainage on Earth (Squyres et al., 2004, and Bibring et al., 2005). Furthermore, the intrinsic association of sulfate minerals with liquid water is consistent with surface or near-surface water being present during Martian history (Elwood et al., 2004). Latest data from Mars Exploration Rovers provide multiple lines of evidence indicating the extensive presence of sulfates on Mars's surface. Measurements by NASA's Mars Pathfinder and Viking landers showed that sulfur is a substantial component of soil dust and surface rocks (Elwood Madden et al., 2004).

![Figure 4](image-url) The Mars rover Opportunity made several stunning discoveries that provide clear evidence for the past presence of liquid water on Mars. These include the occurrence of iron oxide concretions as well as sulfate minerals. The rounded blue-colored spheres in the upper part of the photo are iron oxide concretions (photo credit: Cornell University/NASA). Evidence of hydrated sulfate salt deposits in the Martian tropics comes from near-infrared spectral data on Mars Express.

In addition, sulfates have been identified in Mars meteorites, the SNC group (Shergottites, Nakhliites, Chassignites), which contain salt minerals including sulfates, up to 1% by volume. These evidences taken together strongly suggest that sulfate minerals are on the Mars surface and within the upper lithosphere. Sulfate minerals are a potential archive of information on both the sulfur geochemical cycle and history of water on Mars (Lefictariu et al., 2006b). Sulfate-solutions host diverse microbial communities on the surface and in the subsurface of Earth, lending credence to the search for evidence of extinct or extant life on Mars (Knoll et al., 2005, and Atreya et al., 2006). The chemical and isotopic compositions of Martian sulfate minerals bear valuable clues about past and recent geochemical processes and can help our understanding of the history of water and the potential presence of life on Mars.

References: