

Variation in Photoreactivity of Iron Hydroxides Taken from an Acidic Mountain Stream

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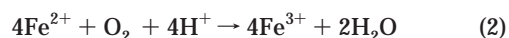
The photoreduction of iron hydroxides is known to exert significant influence over many biogeochemical processes in streams impacted by acid mine drainage. Using laboratory and in-stream measurements, the variation in reactivity of iron hydroxides taken from a stream receiving acid mine drainage (AMD) was studied. The reactivity decreased for material collected at sites progressively downstream from the AMD inflow. In the presence of two simple organic ligands, photoreduction increased for the fresher iron hydroxides but remained unchanged for the older hydroxides. The importance of ligand coordination to the enhancement of photoreduction in natural waters was further demonstrated in experiments using two types of fulvic acids. In-stream measurements of hydrogen peroxide concentration are consistent with the conclusions drawn from the batch experiments. Iron hydroxides were observed to age over time, becoming less photoreactive. This aging was accompanied by an increase in crystallinity. The loss of photoreactivity for the older material can be explained by a decrease in the number of active surface sites, a change in the nature of the surface sites, or a combination of both.

Introduction

The photoreactivity of iron compounds has been recognized for over 100 years. It is somewhat surprising then that the importance of iron photochemistry in natural waters is a relatively recent revelation. Collienne studied the photoreduction of ferric iron in an acidic lake, while others have studied the role of photochemistry on iron speciation in colored-water lakes (1, 2). Waite and Morel used laboratory experiments to define the role of dissolved organic carbon (DOC) in the photodissolution of γ -FeOOH in freshwater and marine systems (3). Iron photochemistry has been postulated to be important in increasing the amount of available iron to organisms in marine environments, where the concentration of DOC is much greater than the concentration of iron.

The importance of iron photoreduction in environments where the iron concentrations exceed concentrations of dissolved organic material has also been demonstrated. McKnight et al. (4) and McKnight and Bencala (5) showed

that the iron hydroxides present in two metal-rich acidic mountain streams undergo photoreductive dissolution. St. Kevin Gulch is a tributary to Tennessee Creek, located near Leadville, CO, and receives acidic metal-laden inflow from several abandoned mines within its watershed. During the night hours, oxidation of the ferrous iron occurs resulting in a reprecipitation of fresh iron hydroxides. Subsequent field experiments have detailed how this diel cycle affects nutrient transport and dissolved organic carbon (6, 7). McKnight and Bencala have also reported the photoreduction/dissolution of iron hydroxides in a second acidic stream, the Snake River near Montezuma, CO (5). The acidity in this stream arises not from the inflow of acidic mine drainage but from the natural weathering of disseminated pyrite in the country rocks of the watershed through a series of reactions shown below:



These same reactions are operating in mine drainage streams. The precipitation of iron hydroxides, (eq 3) results from the rise in pH upon mixing of the acidic mine drainage with neutral streamwater. These hydroxides coat the cobbles and sediment giving the stream bed a characteristic orange color known to miners as "yellowboy".

The diel cycle of photoreduction/dissolution followed by oxidation/precipitation for these materials exerts control over many in-stream processes including trace metal transport. Precipitating iron oxides can remove dissolved fulvic acid from solution due to both coprecipitation and sorption (7). An enhancement in photoreduction has been noted when freshly prepared iron hydroxides are photolyzed in the presence of fulvic acids (3). Coordination of organic matter to the ironhydroxide surface results in an enhanced ligand to metal charge transfer, resulting in the formation of Fe(II) at the hydroxide surface, which is subsequently released to the solution. Another process that will also influence the concentration of dissolved fulvic acid is direct photolysis, which produces hydrogen peroxide (8). The ferrous iron produced by photoreduction may react with H_2O_2 through photoFenton reactions. Thus, the interplay of DOM sorption and photoredox reactions may control the variation of photoreactivity of iron oxides in acidic streams.

To better understand the biogeochemistry of iron hydroxides in an acidic stream, we undertook a project to study their photoreactivity as it relates to age. We conducted laboratory experiments using iron hydroxides taken from St. Kevin Gulch that show that the photoreactivity of the iron oxides in this stream varies spatially. The photoreduction decreases for material taken from sites progressively downstream from the acid mine drainage inflow. The decrease in photoreactivity is associated with an increase in crystallinity and a decrease in sorption capacity of organic ligands over a 3-week period.

Experimental Section

General. Iron hydroxide samples were collected periodically from St. Kevin Gulch throughout the fall of 1995. Collection of the stream bed material was accomplished by first agitating the stream bed and collecting the resulting suspension using

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a turkey baster. The suspensions were stored in amber bottles. An elemental composition of the iron hydroxides from St. Kevin Gulch has been reported (9). Material for the photolysis experiments was isolated by shaking the bottles and filtering the suspension through a 105- μm polypropylene mesh. The filtrate was filtered a second time through a 0.1- μm polycarbonate filter. The iron hydroxides collected on this filter were air-dried and stored in the dark until use. Powder X-ray diffraction spectra were recorded using a Scintag XDS 2000 powder X-ray diffractometer operating with Cu K α radiation. Hydrochloric acid (ACS reagent grade), phthalic acid (ACS reagent grade), and aspartic acid were obtained from Aldrich Chemical Co. and used without further purification.

Photoreactivity Experiments. Photolysis experiments were carried out using an Oriel solar simulator operating at 500 W. A minimum of three replicates was performed for each experiment. Fifteen milligrams of iron hydroxides was added to 50 mL of water in a water-cooled, jacketed beaker. The pH was adjusted to 3.5 using 1.5 M HCl. The photolysis lasted for 1 h, after which time the solution was filtered through a 0.1- μm polycarbonate filter. Analysis for total iron and iron(II) was done using a spectrophotometric method (10). The concentration of iron(III) was taken to be the difference between the total iron and iron(II).

Adsorption Experiments. Phthalic acid adsorption experiments were performed by adding 0.05 g of iron hydroxide to 40 mL of 0.03 mM phthalic acid. The mixture was kept in the dark for 1 h and swirled occasionally. After 1 h, the mixture was filtered through a 0.1- μm filter. The filtrate was analyzed for DOC using a Dohrmann organic carbon analyzer.

Desorption Experiments. A total of 0.01 g of iron hydroxide was dissolved in 50 mL of 0.15 M HCl. The solution was diluted to 100 mL and filtered through a 0.1- μm filter. DOC was determined using a Dohrmann organic carbon analyzer.

Sampling of St. Kevin Gulch. Water samples were collected on September 15, 1995, a partially cloudy day between 12:52 and 14:10. Samples were collected at 11 sites along a 2-km reach downstream from the AMD inflow, filtered using 0.4- μm Nucleopore filters for Fe and H₂O₂ and GFC glass fiber filters for DOC. Hydrogen peroxide samples were stored in polyethylene bottles. DOC samples were stored in amber glass bottles. The DOC bottles and glass fiber filters were muffled prior to use. The samples were analyzed within 48 h of collection. Triplicate analysis of DOC were performed with an average error of 0.05 mg of C/L. Based upon repeat analyses of standards, the error in the iron and hydrogen peroxide analyses was 2–5%. Hydrogen peroxide was determined by a modification of a published method (11). Specifically, the *p*-hydroxyphenylacetic acid concentration was reduced to 75 μM to give a maximum measurable hydrogen peroxide concentration of 50 μM , and the EDTA concentration was increased 10-fold to accommodate the high metals concentration in the stream.

Site Description and Sample Collection

A legacy of Colorado's mining heritage is numerous abandoned mines scattered throughout the mountainous regions of the state. It is estimated that there are 30 000 abandoned mines in the mining district, which runs southwest to northeast from the San Juan Mountains to near Boulder, roughly paralleling the Continental Divide (12). Drainage from these abandoned mines often mixes with surface waters causing significant loss of water quality by discharging acidity and high loadings of heavy metals into stream systems.

St. Kevin Gulch is an ideal site for this study because numerous seeps from the waste rock and tailings pile have been collected through a series of pipes into one main inflow that enters the stream at a point designated as 580 m. The

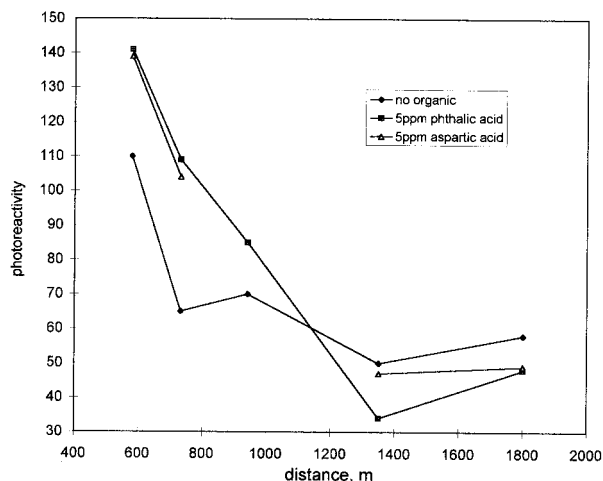


FIGURE 1. Photoreactivity [$(\mu\text{mol of Fe(II)}) (\text{g of hydroxide})^{-1} (\text{h})^{-1}$] of iron hydroxides.

distance measurements are relative to a point upstream from the mine site and study reach. This localized inflow provides an effective point source for the AMD from which iron hydroxides can be collected from progressively farther downstream sites. Iron hydroxides were collected from St. Kevin Gulch at sites designated, 580, 732, 941, 1350, and 1800 m, representing approximately a 1.2 km reach of the stream from the AMD inflow. These materials were used in laboratory experiments to study the photoreduction in more detail.

Results and Discussion

The results of the experiments from the five sites in St. Kevin's Gulch are shown in Figure 1. When the photolysis was carried out in deionized water, the freshest iron hydroxides, the 580-m material obtained from just below the AMD inflow, showed the greatest extent of photoreduction, producing 110 μmol of ferrous iron per gram of sediment in 1 h. The next two downstream sites (732 and 941 m) produced 65 and 70 μmol of Fe(II), respectively. Samples from the two most downstream sites gave 50 and 58 μmol of Fe(II). It is clear from these data that the photoreduction of iron hydroxides along this reach of St. Kevin Gulch varies with location and generally decreases as the distance from the point source increases. The implication is that the age of the iron hydroxides increases downstream and that, as the age increases, the photoreactivity decreases.

We performed experiments to study the effect of added organics on the photoreactivity of St. Kevin material. The results are included in Figure 1. Phthalic acid and aspartic acid were used as models for the ligating sites in dissolved organic carbon. When the photolyses were carried out in 5 ppm phthalic acid, photoreduction increased, but only for the material taken from the upstream sites. The 580 m hydroxides produced 141 μmol of Fe(II) ($\text{g of sediment})^{-1}$. Similar increases were noted for the 732 and 941 m hydroxides. No increase in photoreduction was observed for the 1350 or 1800 m material. In fact, a slight decrease in Fe(II) production was observed. Similar reactivity patterns were observed when the photolysis experiments were carried out in 5 ppm aspartic acid.

There are several hypotheses that can be proposed to account for the observed variations in reactivity. It is known from studies using freshly prepared iron hydroxides that coordination of the organic to the hydroxide surface is a necessary requisite for the enhancement of photoreduction (3). The results of this work using St. Kevin material suggest that the hydroxides from the two downstream sites are

TABLE 1. Effect of Fulvic Acid Type on Iron Hydroxide Photoreduction

medium	site (m)	photoreactivity
		[μmol of Fe(II) ($\text{g}_{\text{sediment}}^{-1}$ (h^{-1})] ($\pm 11 \mu\text{mol}$)
DI water	580	110
	1350	50
5 ppm coordinating fulvic acid	580	139
	1350	39
5 ppm noncoordinating fulvic acid	580	116
	1350	44

incapable of coordinating the phthalic or aspartic acid ligands at surface hydroxide sites. This could be explained by assuming that the older iron hydroxides were already heavily coated with organic material and could not bind the added organic molecules, leading to no photoenhancement. At site 580 m, fulvic acids and other natural organic acids are incorporated into the precipitating iron oxides by both coprecipitation and sorption. Because the DOC of St. Kevin water is low (1.5 mg of C/L or lower) relative to the quantity of precipitating iron hydroxide, we would expect sorption sites on the iron hydroxide to remain available at site 580 m. Over time, as the iron hydroxides are transported downstream, these sorption sites would become occupied by fulvic acid sources coming in with lateral inflows to the stream. To determine if these processes resulted in higher downstream organic contents of the iron hydroxides, a desorption/dissolution experiment was performed. Ten milligram of 580, 941, 1350, and 1800 m material was dissolved in 0.15 M HCl. The dissolved organic carbon concentration was determined. The amount of organic material adsorbed was 4.55%, 5.38%, 5.8%, and 5.32%, respectively. The slightly lower organic content is consistent with these proposed mechanisms but is not definitive. We performed an adsorption experiment to support this conclusion. Fifty milligrams of hydroxide was added to a 5 ppm solution of phthalic acid. After 1 h the mixture was filtered. Analysis of the solution for DOC before and after the addition showed that 1.7 mg of phthalic acid was adsorbed per gram of 580 m hydroxide. The same experiment using 1350 m material showed no change in organic concentration in the solution.

We also performed an experiment, using aquatic fulvic acid, to further probe the requirement that coordination of the organic ligand to the hydroxide surface is necessary for the photoenhancement. Two types of fulvic acids were isolated from the Snake River, a naturally acidic stream located in Summit County, CO. The isolation of these materials has been previously described (7). The fulvic acid that was isolated by dissolving the precipitated hydroxides is known to adsorb strongly, having high aromatic carbon and carboxyl group content. The other fulvic acid remained in solution in the stream and is high in aliphatic carbon and does not adsorb onto iron hydroxides. The results of photolysis experiments in the presence and absence of these fulvic acids are presented in Table 1. It is clear that the ability of the fulvic acid to coordinate to the hydroxide is an important property in order for enhancement of photoreduction to occur. The experiments using 5 ppm coordinating fulvic acid showed a 17% increase in Fe(II) relative to those using water. When a 5 ppm solution of noncoordinating fulvic acid was used, the production of Fe(II) was comparable to that for water, 116 μmol vs 110 μmol . Table 1 includes data with these two fulvic acids and 1350 m material. As can be seen, there is no significant difference between either fulvic acid or water. The uncertainty associated with these measurements is $\pm 11 \mu\text{mol}$ of Fe(II) (g of hydroxide) $^{-1}$ h^{-1} . This is further evidence that the older hydroxides cannot effectively coordinate organic ligands.

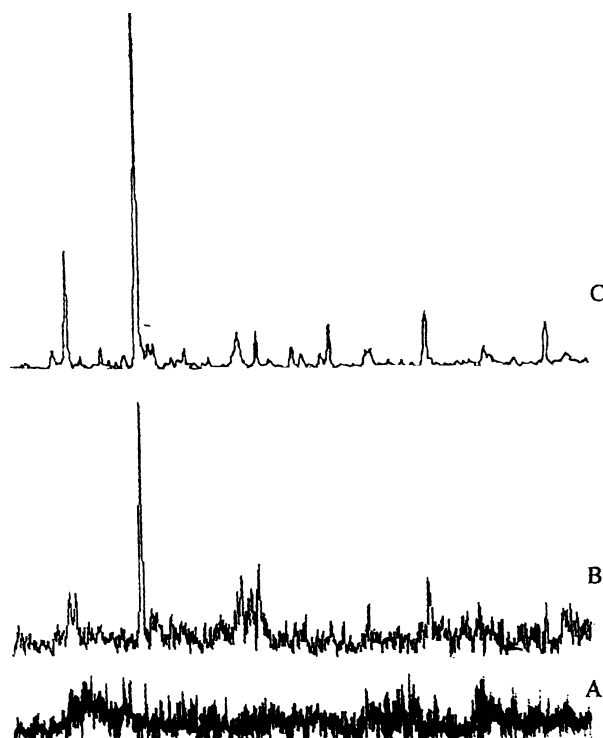


FIGURE 2. XRD spectra of (A) 580 m iron hydroxides, (B) aged 580 m iron hydroxides, and (C) 1350 m iron hydroxides.

During the course of our investigations, we noticed that the freshest materials collected from the 580, 732, and 941 m sites lost activity over a period of weeks. As 580 m hydroxides sat in the dark in air for a period of 3 weeks, the photoreactivity decreased approximately 20%. A sample that had been in the dark in its native streamwater for the 3-week period showed a 40% decrease.

In contrast, there was no aging associated with the 1350 m material. A sample isolated after 3 weeks in its native streamwater produced 48 μmol of Fe(II) as compared to 50 μmol produced by freshly obtained material.

It is known that amorphous synthetic iron hydroxide solutions age to form goethite, hematite, and lepidocrocite (13). Powder X-ray diffraction analysis of freshly obtained 580 m, aged 580 m, and 1350 m hydroxides from St. Kevin Gulch is presented in Figure 2. The fresh 580 m material is amorphous. However, the aged 580 m material shows an increase in crystallinity, having seven observed reflections (7.1° , 12.8° , 21.0° , 22.7° , 28.5° , 36.3° , 46.3°), out to $2\Theta = 50^\circ$. These reflections are also observed, along with others, in the 1350 m material. It is interesting to compare these two patterns to goethite, lepidocrocite, and hematite. Major peaks present in goethite (21.3° , 33.3° , 36.7° , 41.2°), lepidocrocite (14.2° , 27.0° , 36.4° , 46.9°) and hematite (24.1° , 33.2° , 35.6° , 49.5°) are absent in the St. Kevin material. Thus there is no definitive match for these three minerals with the material taken from St. Kevin Gulch, implying that a more complicated iron mineralogy exists in this mine drainage stream. This is consistent with the work of Bigham, who found that the iron hydroxides taken from acid mine drainage associated with coal mines were comprised of a variety of minerals including a poorly crystallized iron oxyhydroxysulfate (14).

An increase in crystallinity is often accompanied by a decrease in surface area. In addition to a possible saturation of organic sorption sites, this could account for the photolysis results, with the older material having fewer active surface sites for photoreduction. No attempt was made to determine the surface area of the various hydroxides because traditional

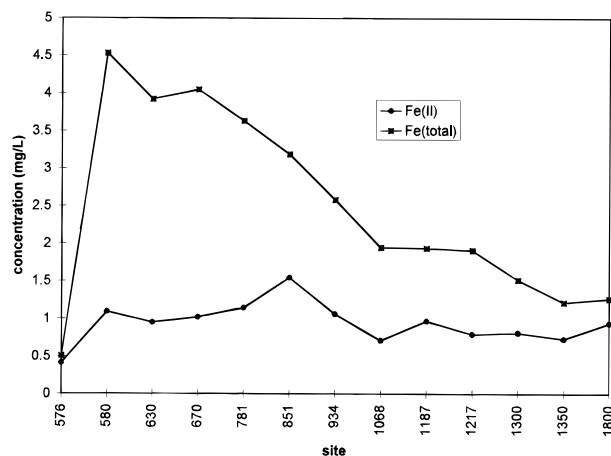


FIGURE 3. Fe(II) and Fe(total) concentrations at 23 sites along St. Kevin Gulch measured during a synoptic sampling.

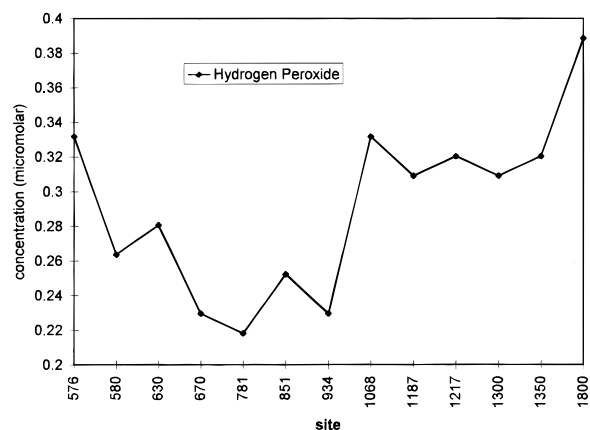
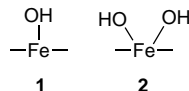


FIGURE 4. Hydrogen peroxide (μM) concentrations at 23 sites along St. Kevin Gulch measured during synoptic sampling.

adsorption methods cause significant alteration of these highly hydrated materials.

Another explanation for a decrease in photoreactivity is that the nature of the surface sites has changed in the older material. In solution phase studies, it has been shown that FeOH^{2+} is more reactive than $\text{Fe}(\text{OH})_2^+$ (15). If similar surface species exist for the hydroxides, then the more highly hydrolyzed site (2) would be expected to be less photoreactive and more inert toward exchange reactions with organic ligands.



We speculate that the older hydroxides in St. Kevin Gulch will have a higher concentration of hydrolyzed sites (2) by virtue of their longer residence time in the stream. Experiments are being planned to study in detail the physical changes in the hydroxides from St. Kevin Gulch that occur with aging.

Figures 3–5 show the downstream variation in total dissolved iron, ferrous iron, DOC, and H_2O_2 measured in St. Kevin Gulch on a partially cloudy day in mid-September. Immediately below the AMD inflow, at 580 m, the DOC and H_2O_2 concentrations decrease abruptly and the total iron and ferrous iron increase. The decrease in DOC can be explained by the sorption of fulvic acid onto the freshly precipitating iron oxides; the decrease in H_2O_2 can be explained by the Fe(II) consuming the hydrogen peroxide

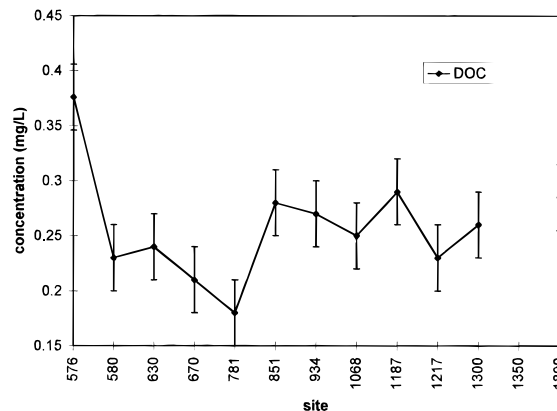


FIGURE 5. Dissolved organic carbon (mg of C/L) concentrations at 23 sites along St. Kevin Gulch measured during a synoptic sampling.

through a photoFenton reaction. Further below the inflow, the ferric iron concentration steadily decreases, but the ferrous iron concentration remains around 1 mg/L. After most of the ferric iron has precipitated, the DOC and H_2O_2 rebound to concentrations above the inflow. Throughout the downstream reach, new DOC is entering the stream from the lateral inflows, from shallow groundwater, and from seeps. However the DOC concentration does not remain suppressed as in the upper reach where iron oxide is abundantly precipitating. These results show that, beyond the reach with abundant iron oxide precipitation, enough of the inflowing DOC remains in the streamwater to be photolyzed, producing hydrogen peroxide.

Stream Scale Implications

In this paper, we have shown that the photoreactivity of iron hydroxides taken from a stream impacted by acidic mine drainage decreases downstream from the AMD inflow. The ability to coordinate organic ligands also decreases. These decreases can be explained by a loss of surface sites due to increasing crystallinity or by a higher concentration of more highly hydrolyzed, less reactive sites or, perhaps, a combination of both. These results have several implications for iron biogeochemistry on a stream scale. One is that, as the iron hydroxides age and are transported downstream, they become less photoreactive, more inert toward reaction with stream DOC, and exert less control over in-stream biogeochemical processes.

Furthermore, these results illustrate the interplay between rates of chemical reactions and rates of hydrologic transport. The rate at which the deposited flocculent amorphous hydroxides are transported downstream relative to the rate at which the hydroxides age controls the extent of photoreduction of stream bed material. It is also interesting to note that the filamentous green alga (*Ulothrix*) which is abundant on the stream bed, is covered with iron hydroxides. Once these hydroxides have aged, they may not be photoreactive and may serve as an armor protecting the green alga from deleterious effects of hydroxyl and organic radicals produced in photoreduction. A final implication is that the formation of more crystalline aged iron oxides that are deposited in sediments removes iron from the in stream iron photoredox cycle. The other loss term is hydrologic transport of dissolved ferrous or ferric iron out of the stream.

Acknowledgments

This research was supported by the USGS Toxic Substances Hydrology Program. We thank E. Carraway, A. Schiller, B. Kimball, and K. Bencala for field assistance and helpful comments.

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Received for review November 7, 1997. Revised manuscript received April 14, 1998. Accepted May 1, 1998.

ES970986L