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Paper

The effect of a diacetylene-containing phospholipid on the oxidation of pyrite, FeS₂, was investigated. Earlier work reported by our research group showed that the adsorption of 1,2-bis(10,12-tricosadiynoyl)-*sn*-glycero-3-phosphocholine on pyrite suppressed the extent of its oxidation by about 75% over a specific time period. Results presented here show that the pre-exposure to UV radiation of this lipid after sorption onto pyrite results in a 90% suppression. Attenuated total reflection (ATR) Fourier transform infra-red spectroscopy (FTIR) suggests that the UV irradiation of the lipid does not result in degradation of the adsorbed layer. It is believed that the UV exposure results in the cross-linking and polymerization of the adsorbed phospholipid into a relatively impermeable barrier that separates the pyrite from the aqueous phase. The results of this study might have implications for the protection of pyrite from oxidation in the environment.

1. Introduction

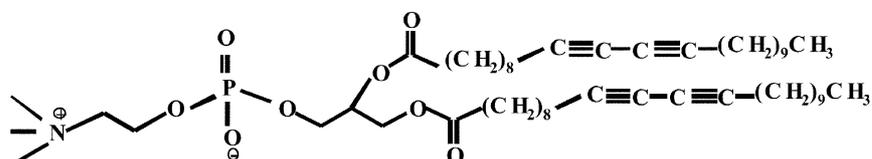
There is significant interest in reducing the amount of metal sulfide oxidation in the environment. Exposure of mine waste containing metal sulfides, such as pyrite, to air and water leads to the formation of acid-mine drainage (AMD).^{1,2} Research in our laboratories has been focused recently on the use of phospholipids to suppress pyrite oxidation. Specifically, it has been shown that phospholipids, containing two long hydrocarbon tails and one polar head group, adsorb readily on pyrite in an aqueous suspension and inhibit the oxidative decomposition of the mineral. At a solution pH of 2, the adsorption of 1,2-bis(10,12-tricosadiynoyl)-*sn*-glycero-3-phosphocholine (23:2 Diyne PC), which has the general structure shown below, decreased the amount of pyrite oxidation by up to 75% when compared to pyrite without adsorbed lipid.³ While the mechanism by which the lipid inhibits pyrite oxidation is not borne out by experiment, research in our laboratories suggest that the formation of a protective lipid bilayer is perhaps an important aspect.⁴ Such a lipid structure would include a hydrophobic pocket to inhibit the interaction of water with the pyrite surface. As we have reported in a series of contributions, water is a key reactant in the oxidation of pyrite.⁵⁻⁷ Hence, the notion is that by creating a hydrophobic layer or partial layer on the pyrite surface, oxidation would be inhibited or at least suppressed. It is mentioned that the investigation of phospholipids as a oxidation suppression agent developed from an earlier observation in our laboratory that showed that phosphate adsorbed alone on pyrite decreased the extent of pyrite oxidation at relatively high pH (>4), but was readily removed at a pH near 2.⁶ It was then hypothesized that the hydrophobic tail of a phospholipid might stabilize the adsorbed phosphate group, that would be expected to bind the lipid to the pyrite surface.

In this contribution we extend our investigation of 23:2 Diyne PC as an adsorbed phase that inhibits pyrite oxidation. Prior studies have shown that the ultra-violet (UV) irradiation of this lipid,⁸ which has diacetylene groups in its hydrocarbon tails, leads to cross linking and polymerization in circumstances where there is a favorable alignment of neighboring lipid molecule tails. The scientific hypothesis in our research is that the cross-linking (*i.e.*, polymerization) will lead to further pyrite oxidation inhibition, relative to the unpolymerized lipid, by providing a significant barrier between the pyrite surface and reactant. To test this hypothesis aqueous batch experiments, which measure the extent of pyrite oxidation with and without lipid, are presented. For reference, it is interesting to note that polymerizable phospholipids have been actively studied because of their biological importance and are often used as models for biomembranes in biochemical research.⁹ Such lipids also have applications as carriers for drugs,⁹ biosensors,^{10,11} artificial red cells¹² and other advanced biomaterials.¹³

2. Experimental

The lipid, 23:2 Diyne PC, was obtained from Avanti Polar Lipids, Inc. in powder form (white). A suspension of 23:2 Diyne PC in water was formed by adding 20 mg of the lipid to 20 mL of deoxygenated 0.10 M NaCl solution. The suspension was sonicated for 30 min to increase the solubility of the lipid and to promote the disruption of large multilamellar vesicles (LMV) that were presumably present in the suspension.

Pyrite powder (BET surface area of 0.75 m² g⁻¹) used in this study was synthesized in our laboratory by a method published elsewhere.¹⁴ Its structure was determined by X-ray diffraction. Prior to its use, the pyrite was exposed to anoxic water at pH 2 (HCl was used to achieve this pH) to remove surface



layers that were oxidized from extended exposure to the ambient atmosphere.⁶ The pyrite was subsequently washed with anoxic water. After this cleaning procedure, 200 mg of the mineral were placed in the lipid suspension in a nitrogen-filled (*i.e.*, oxygen-free) glove bag. After 15 min the supernatant was filtered out leaving behind the lipid-coated pyrite particles. Prior results from our laboratory showed that under these experimental conditions, the amount of lipid adsorbed to the pyrite (1.78×10^{-9} mol mg⁻¹) was estimated to be about 10% more than could be accommodated in a single lipid layer structure. This estimate assumed that the entire pyrite surface was capable of adsorbing lipid and the lipid (with a 70 Å² cross-sectional area¹⁵) adsorbed with its axis along the surface normal. We point out that 2% of the lipid initially in the lipid suspension adsorbed to the pyrite surface, suggesting that the adsorption process was limited by the amount of open pyrite surface.

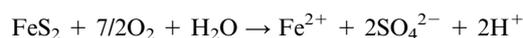
The lipid/pyrite particles were added to 20 mL of deionized (DI) water and this suspension was placed in a quartz container. The suspension was stirred and exposed to the radiation emitted from a 900 W Xe lamp for 150 min at room temperature in a water-cooled quartz container. After exposure to the radiation, the particles were filtered and transferred into 20 mL of pH 2 DI water. Three other types of samples were prepared that were used in our control experiments. In the first, a lipid/pyrite sample was transferred into the pH 2 water without exposure to the Xe lamp. In the second, pyrite without lipid was exposed to the pH 2 water without exposure to lipid or light. Finally, in the third control experiment pyrite without lipid was exposed to UV radiation for 150 min prior to its introduction into the pH 2 DI water.

The extent of pyrite oxidation was determined on the basis of the amount of Fe release into solution as a function of time. Fe release into solution was determined by the ferrozine analytical method.¹⁶ It is pointed out that ascorbic acid was introduced into the sample solution prior to ferrozine introduction to convert any solution Fe(III) into Fe(II). The Fe(II)-ferrozine complex absorbance was monitored with UV-vis spectroscopy (Perkin Elmer) at 560 nm. The solution concentration of Fe(II) was determined by use of a standard curve.

The ATR-FTIR measurements were carried out by placing lipid-covered pyrite (with or without polymerization) on a Ge-45° parallelogram ATR lens. A water/ethanol solution was added sparingly to the powder and the suspension was placed on the ATR crystal. After the liquid evaporated, the resulting pyrite powder adhered well to the Ge surface. A Nicolet 580 research FTIR was used to obtain the vibrational data obtained in this paper. All IR data was recorded at 1 cm⁻¹ resolution with 1028 co-added scans.

3. Results and discussion

The overall composite reaction for pyrite oxidation with water and dissolved oxygen can be written¹⁷ as



Thus, it is implicit in our analysis that the Fe released in our experiments is associated with the pyrite oxidation reactions in solution. Hence, an increase in Fe release implies an increase in pyrite oxidation. Fig. 1 exhibits Fe release vs. time data for pyrite sample prepared in four different ways. Analysis of the data in the figure indicates that for a given time interval the lipid-free pyrite (with or without UV irradiation) surface results in the largest amount of Fe release. Pyrite with an adsorbed layer of 23:2 Dinyne PC exhibits a reduced amount of Fe release than lipid-free pyrite. The amount of Fe release is further reduced for pyrite with adsorbed lipid that was exposed to UV radiation prior to introduction into the pH 2 solution.

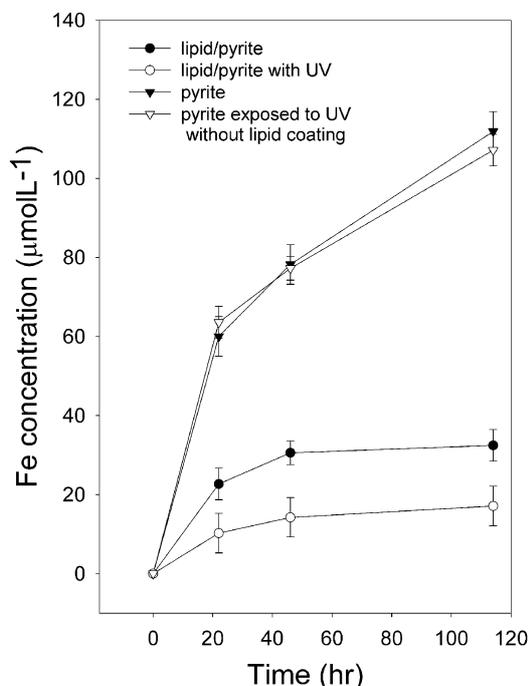


Fig. 1 Fe solution concentration as a function of time for lipid/pyrite, lipid/pyrite with UV, and for two control experiments, pyrite alone, and pyrite that was exposed to UV radiation. The amount of iron release for a given time interval is lowest for the lipid/pyrite surface that had been exposed to UV radiation prior to the start of the Fe release measurements.

As a further control (see figure), iron release from pyrite, which had no adsorbed lipid, but was exposed to UV for the same amount of time as the lipid/pyrite system, was measured to be similar to pyrite without exposure to UV. This result suggests that UV irradiation pretreatment alone does not change the oxidation kinetics of pyrite, within our experimental resolution. As a quantitative example, note that after 120 h the solution Fe concentration for lipid-free pyrite is 118 µmol L⁻¹, while for the same time interval the Fe concentration is 30 and 12 µmol L⁻¹ for the unirradiated lipid/pyrite and irradiated lipid/pyrite samples, respectively. These iron release data suggest that for the same reaction time, the amount of pyrite oxidation is suppressed by 75 and 90% for the unirradiated lipid/pyrite and irradiated lipid/pyrite samples, respectively.

Since a prior publication from our laboratory has already showed that 23:2 Dinyne PC adsorbed on pyrite suppressed oxidation,³ the novel result presented in Fig. 1 is that the exposure of the 23:2 Dinyne PC with UV light leads to a further suppression of pyrite oxidation. Prior studies have shown that the irradiation of the 23:2 Dinyne lipid, which has diacetylenic fatty acyl chains, at a wavelength of 254 nm leads to cross-linking and polymerization in the polymer.⁸ In more general terms, prior research has shown that diacetylenes as a class are often polymerizable under UV irradiation when oriented in mono- or multi-layers.¹⁸⁻²⁰ Furthermore, the resulting conjugated enyne structure in the resulting polymer often leads to a red color. Exposure of pyrite coated with 23:2 Dinyne PC to UV radiation under our experimental conditions also leads to a faint red color easily noticed by a visual inspection of the coated mineral. We also show ATR-FTIR data in Fig. 2 for the lipid/pyrite sample before and after UV irradiation. The before Fig. (2a) and after Fig. (2b) UV exposure spectra are qualitatively similar, suggesting that the UV exposure does not degrade the lipid layer. In short, the inhibition of pyrite oxidation is due to a cross-linked lipid rather than layer of lipid decomposition fragments. Cross-linking within the adsorbed lipid layer through the diacetylene groups of the lipid, presumably described by the following scheme,

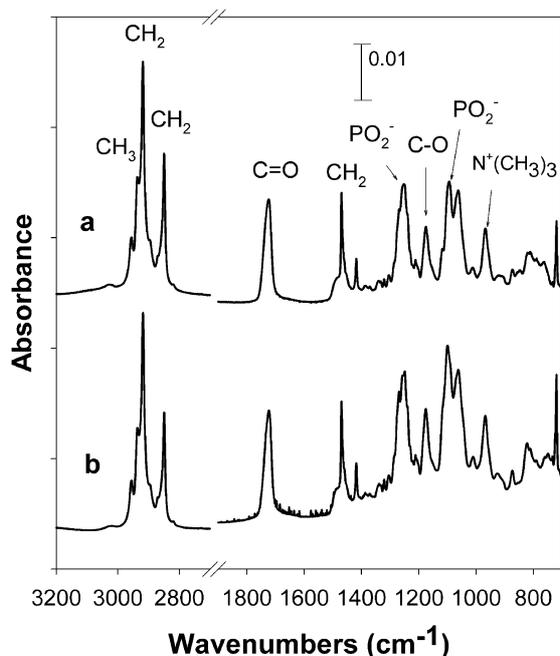
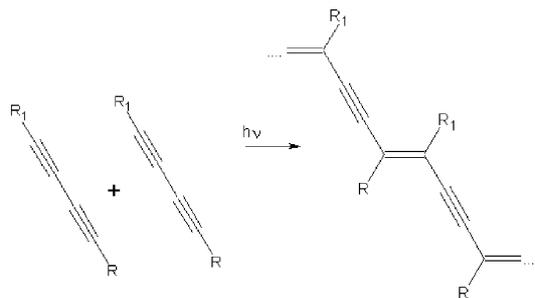


Fig. 2 FTIR of lipid covered pyrite (a) before and (b) after exposure to UV radiation. Association of specific vibrational modes with functional groups of the lipid are indicated.



forms a conjugated structure,⁹ that would not be expected to result in an experimentally observable change in the FTIR spectrum of the lipid.

As mentioned prior research has also suggested that the polymerization occurs with oriented lipid,^{21,22} leading us to speculate that the lipid does adopt a structure on the pyrite surface that is properly aligned to allow the linking. Fig. 3 displays a schematic of what the lipid-surface interaction may resemble. Based on prior research, which investigated the adsorption of phosphate on pyrite,⁶ the phosphate group in the lipid head group binds to the pyrite surface. It is suggested that the hydrophobic nature of the lipid tails might retard pyrite oxidation by decreasing the interaction of the aqueous phase with the pyrite surface. The polymerized film formed during UV exposure is presumably even more impermeable and structurally stable than the adsorbed lipid without UV exposure, further decreasing the penetration of reactant to the pyrite surface. We point out that lipid binding presumably does not need to occur over the entire surface, since prior research has suggested that Fe(III)-containing sites, which make up a fraction of the pyrite surface, are key sites in the initial oxidation of the pyrite surface.⁵ It is pointed out that aqueous Fe(III) is an effective oxidant of the pyrite surface.²³ The aqueous Fe(III) can result from the oxidation of Fe(II) released into solution, and one might surmise that the interaction of this aqueous species with the pyrite surface would also be impeded by the lipid layer.

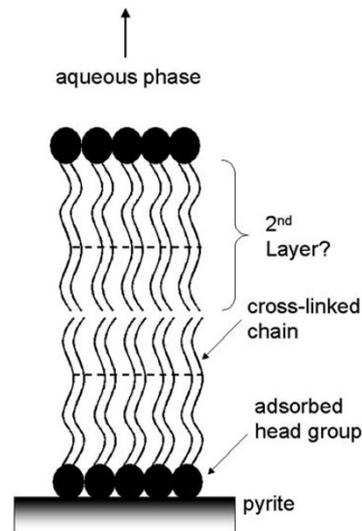


Fig. 3 Schematic representation of a proposed model for the cross-linked lipid/pyrite surface. UV irradiation leads to the cross-linking (indicated by dashed line) and the stabilization of the lipid layer compared to the lipid layer without UV exposure. Whether a bilayer structure forms at the pyrite surface cannot be ascertained from the experimental results.

We are unsure, however, of the specifics of the polymerized lipid structure on the pyrite surface. For example, the relative extent of intermolecular (between adjacent lipids) and intramolecular (within a specific lipid) polymerization is uncertain, but based on the oxidation suppression results, intermolecular polymerization must be significant to form such an effective protective barrier. Also, we cannot completely ascertain from our data whether the lipid forms a bilayer structure at the pyrite surface. However, such an ordered structure would be compatible with the need for an oriented layer for the polymerization to occur.⁹ The amount of lipid adsorbed onto the pyrite, however, was not expected to be enough (see Experimental) to result in the formation of a bilayer structure over the entire surface. If a bilayer structure resulted, we surmise that it would need to be restricted to only a fraction of the total pyrite surface.

4. Summary and general comment

The suppression of pyrite oxidation, a significant cause of acid-mine drainage, has been addressed. Prior studies showed that the adsorption of 1,2-bis(10,12-tricosadiynoyl)-*sn*-glycero-3-phosphocholine on pyrite significantly decreased the oxidation of the mineral in the aqueous environment. Results presented in this paper showed that the exposure of the lipid to UV radiation prior to oxidation led to the polymerization of the diacetylene groups in the lipid tails. Creation of this cross-linked layer on the mineral surface resulted in a suppression of pyrite oxidation by about 90% under our experimental conditions. Whether these lipids will show a similar suppression of pyrite oxidation in the environment cannot be directly inferred from the results presented here. The long-term stability of the lipids supported on pyrite in real AMD environments still needs to be addressed in the future.

Acknowledgements

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References

- 1 B. Eberling, R. V. Nicholson and J. M. Scharer, A combined kinetic and diffusion model for pyrite oxidation in tailings: a change in controls with time, *J. Hydrol.*, 1994, **157**, 47–60.
- 2 D. Banks, P. L. Younger, R.-T. Arnesen, E. R. Iverson and S. B. Banks, Mine-water chemistry: the good, the bad and the ugly, *Environ. Geol.*, 1997, **32**(3), 157–174.
- 3 A. Elsetinow, M. Borda, D. R. Strongin and M. A. Schoonen, Suppression of pyrite oxidation in acidic aqueous environments using lipids having two hydrophobic tails, *Adv. Environ. Res.*, 2003, in press.
- 4 X. Zhang, M. Borda, M. A. Schoonen and D. R. Strongin, The adsorption of phospholipids on pyrite and its effect on surface oxidation, *Langmuir*, 2003, submitted.
- 5 J. M. Guevremont, J. Bebie, A. R. Elsetinow, D. R. Strongin and M. A. A. Schoonen, Reactivity of the (100) Plane of Pyrite in Oxidizing Gaseous and Aqueous Environments: Effects of Surface Imperfections, *Environ. Sci. Technol.*, 1998, **32**, 3743–3748.
- 6 A. R. Elsetinow, M. A. A. Schoonen and D. R. Strongin, Aqueous geochemical and surface science investigation of the effect of phosphate on pyrite oxidation, *Environ. Sci. Technol.*, 2001, **35**, 2252–2257.
- 7 M. A. A. Schoonen, A. Elsetinow, M. Borda and D. R. Strongin, Effect of temperature and illumination on pyrite oxidation between pH 2 and 6, *Geochem. Trans.*, 2000, **1**, 23.
- 8 J. H. Georger, A. Singh, R. R. Rice, J. M. Schnur, P. Yager and P. E. Schoen, Helical and tubular microstructures formed by polymerizable phosphatidylcholines, *J. Am. Chem. Soc.*, 1987, **109**, 6169–6175.
- 9 H.-H. Hub, B. Hupfer, H. Koch and H. Ringsdorf, Polymerizable Phospholipid analogues - New stable biomembrane and cell models, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 938.
- 10 P. Yager, J. Person and K. Seib, Development of ion-channel based biosensors using polymerizable lipids, *Proceedings of the Annual International Conference of the IEEE Engineering in Medicine and Biology Society, IEEE*, 1988, **2**, 799–800.
- 11 D. Nikolelis and M. Mitrokotsa, Stabilized lipid film based biosensor for atenolol, *Biosens. Bioelectron.*, 2002, **17**, 565–72.
- 12 F. Hosoi, H. Omichi, K. Akama, K. Awai, S. Endo and Y. Nakano, Radiation-induced polymerization of unsaturated phospholipid mixtures for the synthesis of artificial red cells, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 1997, **131**, 329–34.
- 13 A. Singh, M. Markowitz and G. Chow, Materials fabrication via polymerizable self-organized membranes: an overview, *Nanostruct. Mater.*, 1995, **5**, 141–153.
- 14 J. Bebie, M. A. A. Schoonen, M. Fuhrmann and D. R. Strongin, Surface charge development on transition metal sulfides: an electrokinetic study, *Geochim. Cosmochim. Acta*, 1998, **62**, 633–642.
- 15 R. D. Hunt, M. L. Mitchell and R. A. Dluhy, The interfacial structure of phospholipid monolayer films: an infrared reflectance study, *J. Mol. Struct.*, 1989, **214**, 93–109.
- 16 L. L. Stookey, Ferrozine - a new spectrophotometric reagent for iron, *Anal. Chem.*, 1970, **42**, 779–81.
- 17 M. A. Williamson and J. D. Rimstidt, The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation, *Geochim. Cosmochim. Acta*, 1994, **58**, 5443–5454.
- 18 G. Lieser, B. Tieke and G. Wegner, Structure, phase transitions and polymerizability of multilayers of some diacetylene monocarboxylic acids, *Thin Solid Films*, 1980, **68**, 77–90.
- 19 B. Tieke, G. Lieser and G. Wegner, Polymerization of diacetylenes in multilayers, *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 1631–44.
- 20 B. Tieke, H. J. Graf, G. Wegner, B. Naegele, H. Ringsdorf, A. Banerjee, D. Day and J. B. Lando, Polymerization of mono- and multilayer forming diacetylenes, *Colloid Polym. Sci.*, 1977, **255**, 521–531.
- 21 E. Lopez, D. F. O'Brien and T. H. Whitesides, Structural effects on the photopolymerization of bilayer membranes, *J. Am. Chem. Soc.*, 1982, **104**, 305–307.
- 22 P. E. Schoen, P. Yager, J. P. Sheridan, R. Price and J. M. Schnur, Order in diacetylenic microstructures, *Mol. Cryst. Liq. Cryst.*, 1987, **153**, 357–366.
- 23 C. O. Moses, D. K. Nordstrom, J. S. Herman and A. L. Mills, Aqueous pyrite oxidation by dissolved oxygen and by ferric iron, *Geochim. Cosmochim. Acta*, 1987, **51**, 161–1572.