THE EFFECT OF VISIBLE LIGHT AND PHOSPHATE ON THE KINETICS OF PYRITE OXIDATION BY DISSOLVED MOLECULAR OXYGEN. Martin Schoonen¹ and Daniel Strongin², ¹Department of Geosciences, SUNY-Stony Brook, Stony Brook, NY 11794-2100, MSCHOONE@NOTES.CC.SUNYSB.EDU, ²Department of Chemistry, Temple University, Philadelphia, PA 19122, DSTRONGI@NIMBUS.OCIS.TEMPLE.EDU.

Introduction: Pyrite oxidation by dissolved O₂ is an important reaction in the global cycles of S and Fe. Mining of sulfide ore and coal has greatly enhanced the global importance of this reaction and has created extremely acid and metal-rich environments. A large number of researchers, including Barnes and McKibben [1], have conducted experimental studies to determine the rate and mechanism of this process so that effective abatement strategies may be developed. Here the effect of illumination and addition of phosphate on the rate of pyrite oxidation is reported. Acid cleaned, crushed pyrite was used. Experiments were conducted in a 1L, water-jacketed, Pyrex, airtight vessel mounted on an optical bench. After pre-equilibrating the pyrite for 6 to 12 hours in O₂-free water, pure O₂ gas was admitted. (The pre-equilibration is necessary to obtain reproducible results, we think that during this period intrinsic defects react with water; this notion is based on earlier UHV work [2]). The pH was kept constant using a pH-stat and the amount of NaOH added was used as a progress variable. Sulfate, Fe₄₋, and PO₄ were periodically measured on aliquots. After establishing the reaction rate with the vessel covered with a black plastic sheet, the vessel was uncovered and illuminated with a 1000 Watt Xenon lamp. The beam was cooled by passing it through a water filter. After establishing the rate under illumination, the vessel was covered again and the rate in the dark was re-measured. Experiments were carried out at pH 3, 4, 5, and 6. The temperature was closely monitored and all experiments were conducted at a temperature between 24 and 28°C. To evaluate the effect of PO₄ addition two experiments were conducted at pH 4 and 6 in which the oxidation rate in the dark was measured as a function of PO₄ concentration.

Results and Discussion: Illumination accelerates the reaction rate by a factor of five at pH 3, 2.5 at pH 4 (see Figure), a factor of 1.13 at pH 5, and a factor of 1.4 at pH 6. However, the rate of acid generation at pH 5 and 6 is nearly a factor of ten higher than at pH 3 and 4. In all experiments, except the one at pH 5, a period of no acid generation was observed after the lamp was turned off. After this induction period, which lasted for 16 hours at pH 3, the rate of acid production returned to approximately the same value as before the illumination. Illumination of the pyrite slurry raises the temperature in the vessel almost instantaneously a few degree C due to the fact that pyrite can absorb part of the radiation. This increase in heat cannot be efficiently dissipated even though the vessel is cooled by a constant temperature water bath. Given the high activation energy for pyrite oxidation, the rise in T can explain the slight acceleration at pH 5 and 6, but it cannot account for the acceleration observed at pH 3 and 4. In these most acid experiments, the relative rates of proton production and sulfate production also change when illuminated, suggesting a change in reaction mechanism. Experiments using XPS on single crystals may provide further insight.

A radiation-induced acceleration of pyrite oxidation could lead to a diurnal effect in natural environments and it may explain some of the scatter in reported reaction rates. In general, illumination should be considered as a potentially important variable in any experimental study that involves semi-conducting minerals.

Addition of phosphate decreases the oxidation rate significantly. The retardation effect on the oxidation rate appears to follow a Langmuir adsorption model. Earlier work in our group has shown that little phosphate sorbs on clean pyrite surfaces [3]. On oxidized pyrite surfaces PO₄ can also sorb onto Fe-(hydr)oxide patches. These patches are thought to facilitate electron transfer between the oxidant and the pyrite [2,4]. We postulate that sorption of PO₄ on these patches interferes with the electron transfer and that this is the cause for the retardation.

![Graph showing the effect of illumination on pyrite oxidation.](image)

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