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The Influence of Light and Heat on Pyrite Oxidation between pH 2 and 6

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Pyrite oxidation by dissolved O_2 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. In this study we have examined in detail the effects of light and heat on the reaction rate in solutions with a pH between 2 and 6. Experiments were conducted in a 1L, water-jacketed, Pyrex, airtight vessel mounted on an optical bench. Water from a constant water bath equipped with a cooling unit as well as a heater was pumped through the water jacket. After pre-equilibrating the pyrite for 6 to 12 hours in O_2-free water, pure O_2- gas was admitted. During this initial stage intrinsic defects react with water. The pH was kept constant using a pH-stat and the amount of NaOH added was used as a progress variable. Sulfate and Fe_{tot} were periodically measured on aliquots. After establishing the reaction rate with the vessel covered with a black plastic sheet over a temperature range from 20 to 45 °C, the vessel was uncovered and the measurement over the same temperature range were repeated while the slurry was illuminated with a 1000 Watt Xenon lamp. The beam was cooled by passing it through a water filter. Complementary XPS experiments were conducted with the same level of illumination as in the batch sorption experiments to evaluate the effect of illumination on the composition of the pyrite surface. The rate of the oxidation of pyrite is strongly dependent on temperature. It is, however, not possible to cast the temperature dependence in a simple Arrhenius equation because the magnitude of the activation energy depends on the progress variable chosen. Activation energies based on proton release rate, sulfate release rate, and total iron release rate vary by as much as 40 kJ mol^{-1}, suggesting that the oxidation mechanism of the sulfur and iron component of pyrite are largely independent of each other. This difference in mechanism can also explain why the reaction rates on the basis of these three different progress variables do not show the same pH dependence. Exposed to visible light, the rate of pyrite oxidation is under most conditions accelerated by less than a factor of two. Some of this acceleration may be accounted for by a light-induced heating of the pyrite surface. Surface science experiments employing photoelectron spectroscopy show no evidence for significant changes in the chemical composition of the surface as a function of exposure to visible light. The batch sorption experiments show, however, that the reaction stoichiometry changes somewhat, which indicates that there might be a change in reaction mechanism as a result of exposure to visible light.

Perhaps it is not surprising that in a process with many sequential steps the calculated activation energy differs depending on the choice of progress variable. Unless all species used as progress variables undergo identical elementary steps, the activation energy calculated based on different progress variables may be different. Because geochemical processes are often complex multi-step processes it is likely that for many the determination of activation energies depends on the choice of progress variable.