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The Role of Pyrite in Reactive Oxygen Species Cycling on the Early Earth

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Photochemical iron oxidation [1] combined with pyrite weathering has been proposed as a source of H_2O_2 and other reactive oxygen species (ROS), which may have acted as oxidants in anoxic early oceans. However, the extent and mechanism of ROS production during pyrite weathering has been ambiguous, showing significant variability across different experiments [2-5]. To better constrain this process, we developed a flow-through reactor system combined with high-sensitivity chemiluminescence measurements of H_2O_2 [6]. Rigorous testing allowed us to eliminate the influence of Fe^{2+} on H_2O_2 detection —a factor that has likely led to false positives in past studies [7]. We performed pyrite oxidation experiments under varying O_2 and H_2O_2 inflow concentrations, light intensities, and pyrite loadings. Our results reveal that pyrite oxidation does not lead to net H_2O_2 production; instead, H_2O_2 is always consumed during the oxidation process. From these observations, we derived a rate law for pyrite oxidation as a function of O_2 and H_2O_2 concentrations. On the early Earth, H_2O_2 produced via quartz surface abrasion [8] and silicate erosion [9] may have contributed substantially to ROS availability, acting as an effective oxidant for pyrite alongside Fe^{3+}. Under anoxic conditions in 10 μM H_2O_2 solutions — concentrations that were suggested to be generated by oxidative weathering on Archean continents [9] — we measured sulfate production rates of 1×10^{-9} mol m^{-2} s^{-1}, comparable to rates observed in 1.5 mM irradiated ferrous iron solutions [1]. These results highlight the critical role of pyrite-H_2O_2 interactions in sulfate generation and ROS cycling, offering new insights into nutrient availability and redox dynamics crucial for early life evolution.

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