Quantifying Fenton reaction pathways driven by self-generated H$_2$O$_2$ on pyrite surfaces

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Oxidation of pyrite (FeS$_2$) plays a significant role in the redox cycling of iron and sulfur on Earth and is the primary cause of acid mine drainage (AMD). It has been established that this process involves multi-step electron-transfer reactions between surface defects and adsorbed O$_2$ and H$_2$O, releasing sulfoxy species (e.g., S$_2$O$_3^{2-}$, SO$_4^{2-}$) and ferrous iron (Fe$^{2+}$) to the solution and also producing intermediate by-products, such as hydrogen peroxide (H$_2$O$_2$) and other reactive oxygen species (ROS), however, our understanding of the kinetics of these transient species is still limited. We investigated the kinetics of H$_2$O$_2$ formation in aqueous suspensions of FeS$_2$ microparticles by monitoring, in real time, the H$_2$O$_2$ and dissolved O$_2$ concentration under oxic and anoxic conditions using amperometric microsensors. Additional spectroscopic and structural analyses were done to track the dependencies between the process of FeS$_2$ dissolution and the degradation of H$_2$O$_2$ through the Fenton reaction. Based on our experimental results, we built a kinetic model which explains the observed trend of H$_2$O$_2$, showing that FeS$_2$ dissolution can act as a natural Fenton reagent, influencing the oxidation of third-party species during the long term evolution of geochemical systems, even in oxygen-limited environments.

The chemical and electrical properties of pyrite (FeS$_2$) – the most common iron disulfide in the Earth’s crust – make it a promising material for the construction of photovoltaic panels$^1$, as well as for wastewater remediation$^2$–$^7$. In the last decades, a number of experimental and field studies have addressed the oxidative dissolution of pyrite, providing an accurate characterization of the processes$^8$–$^{17}$. Recent investigations have shown that, aside from the iron and sulfoxy species released during pyrite dissolution, ROS are always present as transient by-products, both under oxic and anoxic conditions$^{18}$–$^{26}$, and providing an important path to oxidize third-party species through oxygen evolution reaction (OER)$^{18}$–$^{27}$.$^{30}$

The rupture of S-Fe and S-S bonds over pyrite surface by mechanical fracture or during the dissolution process induces the formation of the non-stoichiometric defect sites (i.e., the dangling bonds) that trigger adsorption reactions$^{31}$–$^{33}$. The iron surface species formed cause a reduction in the band gap of the pyrite from 0.86 electron volts (eV) in the bulk to 0.55 eV on the surface$^{14}$, catalyzing the dissociation of adsorbed oxygen (O$_2$) and water (H$_2$O) molecules and leading to the formation of H$_2$O$_2$ (equations 1–4)$^{19,25,26,35}$:

\[
\equiv Fe^{2+}_{(surf)} + O_2(g) \rightarrow \equiv Fe^{3+}_{(surf)} + O_2^{*} \tag{1}
\]

\[
\equiv Fe^{2+}_{(surf)} + O_2^{*} + 2H^+ \rightarrow \equiv Fe^{3+}_{(surf)} + H_2O_2_{(aq)} \tag{2}
\]

\[
\equiv Fe^{3+}_{(surf)} + H_2O \rightarrow \equiv Fe^{2+}_{(surf)} + OH^*_{(ad)} + H^+ \tag{3}
\]

\[
OH^*_{(ad)} + OH^*_{(ad)} \rightarrow H_2O_2_{(aq)} \tag{4}
\]

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At the same time, pyrite releases Fe$^{2+}$ into solution than can catalyze the Fenton and Haber-Weiss reactions, leading to the generation of other ROS (equations 5–8)\textsuperscript{4,22,25,26}:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{Fe}^{2+} &\rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \\
\text{H}_2\text{O}_2 + \text{Fe}^{3+} &\rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^* \\
\text{HO}_2^* &\rightarrow \text{O}_2^- + \text{H}^+ \\
\text{O}_2^- + \text{H}_2\text{O}_2 &\xrightarrow{\text{Fe}^{2+}/\text{Fe}^{3+}} \text{OH}^- + \text{O}_2 + \text{OH}^- 
\end{align*}
\]

Although this sequence of reactions describes the basic features of H$_2$O$_2$ formation during pyrite dissolution (equations 1–4) and its further degradation to secondary ROS in solution (equations 5–8), various important aspects remain unclear, for instance: (1) can free radicals be formed by mechanism other than the photoactivation (i.e. by mechanical bond fracture or non-stoichiometry dissolution of pyrite)? (2) can the formation of H$_2$O$_2$ occur in strictly anoxic conditions overcoming the energy required to split the water molecule and the further release of O$_2$? and (3) can the process of ROS generation by pyrite be sustained over long periods of time?.

Real-time measurements of this process are made difficult by ROS reactivity and the subsequent redox transformations of iron and sulfur species. Spectroscopic and fluorescence methods are commonly used to measure the concentration of H$_2$O$_2$; however, these methods usually need the presence of dyes or chelating agents that are not well suited for the kinetic analysis of transient phases. In this study, we measured the real-time generation and decomposition of H$_2$O$_2$ and dissolved O$_2$ induced by pyrite surfaces under different boundary conditions (i.e., dark/light, oxic/anoxic) to investigate the kinetic role of ROS during pyrite dissolution. In addition, we analyzed both the chemical evolution of dissolved species and surface pyrite oxidation with spectroscopy (UV-Vis, XPS), Cyclic Voltammetry (CV) and high-resolution transmission electron microscopy (HTREM) and performed specific experiments to evaluate the persistence of H$_2$O$_2$ formation. Based on our results, we developed a kinetic model for the coupling between pyrite dissolution and H$_2$O$_2$ generation/degradation through the Fenton reaction. When combined with the observed trends this model leads to the definition of constraints on the overall process of ROS oxidation mechanism induced by pyrite surfaces.

**Results**

**H$_2$O$_2$ and O$_2$ evolution: general pathway.** Figure 1 shows the concentration of H$_2$O$_2$ as a function of time in aqueous suspensions of pyrite starting at circumneutral pH, under oxic and anoxic conditions. H$_2$O$_2$ concentration increased at the beginning of the experiment until a maximum value was reached, and decreased thereafter asymptotically towards a nearly stationary, residual value ([H$_2$O$_2$] $>$ 200 nM) still measurable at the end of the experiment (~22 h). This coupled generation-decay response was generally observed in every experiment, although there were variations in the particular shape of the curves and, some experiments showed characteristic shoulders or secondary maxima at intermediate stages of the process. The overall process followed a sigmoidal trend, suggesting a strong interaction between the H$_2$O$_2$ generation and degradation rates characteristic of an autocatalytic process. H$_2$O$_2$ formation and decomposition evolved more slowly under anoxic than under oxic conditions. We did not observe any correlation between pyrite loading and the H$_2$O$_2$ yield between experimental runs under our experimental conditions (i.e., 0.5–0.3 g/L, unbuffered neutral pH) because of several factors (e.g., kinks, steps, lattice anisotropy) can determine the variability of the reactive surface between samples\textsuperscript{36–39}.

The evolution of O$_2$ under anoxic conditions was characterized by an asymptotic decrease followed by a slight increase and a steady stable period at the end of the experiment (Supplementary Fig. S1). The opposite trend was observed under oxic conditions (i.e., an initial increase in O$_2$ followed by an asymptotic decrease). To clarify the role of O$_2$ over the formation of H$_2$O$_2$, we monitored simultaneously the evolution of O$_2$, and H$_2$O$_2$ under oxic
and anoxic conditions (Fig. 2). In oxic conditions (Fig. 2a), the amount of H$_2$O$_2$ increased whereas O$_2$ was rapidly consumed at the beginning of the experiment. Under anoxic conditions O$_2$ and H$_2$O$_2$ formed concomitantly (Fig. 2b).

During the experiments, pH became acidic under both oxic and anoxic conditions. Overall, pH dropped rapidly towards a nearly constant value approximately 2 to 3 pH units lower then at the initial pH value. The initial drop was more pronounced under anoxic than under oxic conditions (2 hours vs 10 hours, respectively), and in both cases the initial decline in pH values was accelerated with increasing pyrite loading (Supplementary Fig. S2).

**The Fenton reaction in anoxic conditions: spectroscopic experiments.** To determine if the Fenton reaction was actually the mechanism to degrade the H$_2$O$_2$ forming under anoxic conditions, we monitored the production of Fe$^{3+}$ and OH· species in pyrite suspensions under anoxic conditions and in the dark (Fig. 3). First, we evaluated the intensity of the absorbance bands in the UV-Vis range of 260–700 nm to identify the formation of dissolved Fe$^{3+}$-complexes that coexist in solution in the range 300–450 nm$^{40–43}$ (Fig. 3a). The first absorbance peak ($\lambda$$_{max}$ ~375 nm) evolved after three hours of reaction and was shifted to higher wavelengths (around 390–400 nm), as the reaction proceeded. Second, we monitored the formation of short-lived radicals, mainly OH· by measuring the decrease in the light absorption spectrum ($\lambda$$_{max}$ = 590 nm) of Crystal Violet used as a dye probe$^{44}$ (Fig. 3b). The absorption spectrum of CV showed a rapid decline indicating that OH· formation occurs concomitantly from the start-up of the experiment.

**Tracking the reversibility of H$_2$O$_2$ generation: cycling experiments.** We performed these experiments to better understand the long-term evolution of H$_2$O$_2$ during pyrite dissolution in an open system. In order to use the same physical pyrite particles and in the same geometry, pyrite microparticles were adhered over silicone strips to form a thin film which was placed on the internal wall of the reactor as in the spectroscopic experiments. We monitored the evolution of H$_2$O$_2$ until the observable amount of H$_2$O$_2$ attained a constant value or a concentration of zero (Fig. 4). At that point, we replaced the solution inside the batch reactor with distilled H$_2$O, and monitored the evolution of H$_2$O$_2$ again (we repeated this procedure twice). After a full cycle of H$_2$O$_2$ generation and decay, the formation of H$_2$O$_2$ was found to resume after the addition of fresh distilled H$_2$O, although the maximum H$_2$O$_2$ yield was consistently lower than in the previous cycle (Fig. 4a). Assuming a zero-order kinetic model, the initial observed rate of the H$_2$O$_2$ formation ($k_0$ obs) showed a slight decrease between the first and the second cycle, which was more prevalent in the third cycle (Fig. 4b). This decrease could be attributed to the formation of oxide patches on pyrite surface that partially block some of the iron reactive centers.

**Surface characterization (CV, XPS and HRTEM).** Results of cyclic voltammetry under anoxic conditions revealed the anodic peaks associated with H$_2$O oxidation by one electron and by two electron transfer (Supplementary Fig. S3). Interestingly, in the cathodic counterpart, the peak assigned to iron reduction is split into two peaks (0.1 V NHE and 0.2V NHE, respectively), indicating that a fraction of Fe$^{3+}$ is reduced in a nearly spontaneous manner. The analyzed XPS spectra of the (001) face of pyrite after aqueous reaction in the presence and absence of dissolved O$_2$ (g) resulted in significant differences, showing major surface oxidation under oxic conditions with the subsequent formation of patches (Supplementary Fig. S4). In fact, XPS analysis of the (100) face of the pyrite after anoxic reaction only showed appreciable changes in the O1s orbital showing a shift to
lower binding energies associated with an increase of the hydroxyl contribution (−OH) (Supplementary Fig. S5). In order to facilitate the identification of ≡SS and ≡Fe3+ dangling bonds, one sample was ion-sputtered, which promoted the breakage of the S-S dimers (as in the grinding procedure) (Supplementary Fig. S6). The formation of iron oxidation patches was also observed with HRTEM. Figure 5 shows an image of the pyrite surface after 22 hours of reaction in a micromolar solution of H2O2 in absence of O2(g). The presence of discrete oxidation patches was observed in the uppermost area of the micrograph (Fig. 5a). The FFT proved that the lattice fringe spacing of low contrast clusters (~0.25 nm) were consistent with ferrihydrite nanocrystals viewed down [001] (Fig. 5b). Additional HRTEM images (Supplementary Fig. S7) also showed the interplanar spacing characteristic of two-line ferrihydrite45,46. The FFT of the crystalline part showed the interplanar spacing of pyrite but also of goethite, suggesting that ferrihydrite can be a precursor of goethite formation (Fig. 5c)47.

Fitting the experimental data: kinetic modeling of H2O2 evolution. Our experimental data suggests that the observed trend of H2O2 is the result of the coupling between the H2O2 generation by iron defect sites on the pyrite surface and the H2O2 decomposition by the Fenton reaction. Based on these results, we built a kinetic model that allowed us to analyze the process in terms of elementary reactions and to determine the specific rate constant of the H2O2 formation in oxic and anoxic conditions by fitting the experimental data. In summary, the model describes the net amount of H2O2 according with the following expression (Supplementary, Modeling approaches):

\[
\text{H}_2\text{O}_2 = \text{constant} \times \text{rate} \times \text{time}
\]

Figure 3. Spectroscopic monitoring of Fe3+ and OH· from pyrite slurries under anoxic conditions. (a) Absorption bands detected from aqueous pyrite suspension in anoxic conditions and in the dark showing Fe3+-complexes signatures (particle loading = 0.28 g/L). The numbers inserted over the absorption bands show the reaction time. Spectra were registered in real time using a liquid waveguide capillary flow cell (LWCC; path length: 250 cm; WPI), connected to the batch reactor by a peristaltic pump; (b) Degradation of CV solution upon pyrite aqueous reaction under anoxic conditions and in the dark (particle loading = 0.12 g/L, [CV]0 = 225.5 μM).

Figure 4. Recurrence of H2O2 formation by pyrite slurry after H2O renewal. (a) H2O2 evolution from the same pyrite slurry after renewing H2O twice, in oxic-open conditions (pyrite load particle = 0.33 g/L, ΔpH1cycle = 6.8–3.8, ΔpH2cycle = 6.8–6.1, ΔpH3cycle = 6.8–6.7); (b) Initial observed rate of H2O2 formation assuming a zero kinetic order rate.
Where \( k_1, k_2 \) and \( k_3 \) represent the rate constants of each Fenton reaction step (Supplementary Table S1). As shown in the equation, the \( \text{H}_2\text{O}_2 \) formation was calculated assuming a first order dependence on the reactive surface and, both iron defect sites act simultaneously, but in anoxic conditions the \( \text{H}_2\text{O}_2 \) produced by Fe\(^{2+}\) sites is limited by the \( \text{O}_2 \) derived by the Fenton reaction. Minimization between experimental curves and the values calculated from equation 9 were made with a non-linear least squares approach using the Marquardt algorithm, with \( k_{\text{oxic}} \) and \( k_{\text{anoxic}} \), the specific rate constants of \( \text{H}_2\text{O}_2 \) surface generation, as adjustable parameters (Table 1).

Figure 6 presents the fitted values corresponding to the evolution of \( \text{H}_2\text{O}_2 \) in oxic and anoxic conditions together with the model derived results. Under oxic conditions (Fig. 6a), when pH was higher, the ferrous surface iron was oxidized by dissolved \( \text{O}_2 \) forming \( \text{H}_2\text{O}_2 \) according the first order rate. Deviations of the linearity started to occur due to a change in the reaction stoichiometry by the simultaneous decrease in pH and increase in dissolved \( \text{Fe}^{2+} \) and \( \text{H}_2\text{O}_2 \). From this point, the Fenton reaction became important and the oxidation rate of \( \text{Fe}^{2+} \) by \( \text{O}_2 \) slowed down leading to a minor \( \text{O}_2 \) consumption. As a result, reactions forming ROS – catalyzed by \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) – became effective for \( \text{H}_2\text{O}_2 \) degradation, which rapidly decreased, while iron species followed an opposite trend. Under anoxic conditions (Fig. 6b), the formation of \( \text{H}_2\text{O}_2 \) proceeded more slowly. The decomposition of \( \text{H}_2\text{O}_2 \) was also retarded because the concentration of dissolved [Fe\(^{2+}\)] supplied to solution by pyrite dissolution was lower. The Fenton reaction was initiated when pH values dropped below 4.5 and the ratio \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) increased, catalyzing the \( \text{H}_2\text{O}_2 \) decomposition similar to the oxic experiments. The analysis of ROS derived from the model in both oxic and anoxic conditions (Fig. 6c and d) shows that, the first reactive species formed was \( \text{OH} \) acting as a chain initiator, forming additional free radicals. The majority of the \( \text{OH} \) reacted with \( \text{H}_2\text{O}_2 \), generating \( \text{HO}_2^- \), the conjugate acid of \( \text{O}_2^- \), which is the limiting reagent to assist the redox cycling of Fe\(^{3+}/\text{Fe}^{2+}\) forming \( \text{O}_2 \) and helping to buffer the pH drop.

Contrary to the expectation, the maximum amount of \( \text{H}_2\text{O}_2 \) measured was significantly different between experimental runs, and independent of particle loading. This was likely because the effect of increasing the reactive surface was twofold: (i) an increase in the formation of \( \text{H}_2\text{O}_2 \), and (ii) an increase in the release of dissolved Fe\(^{2+}\), accelerating the decomposition of \( \text{H}_2\text{O}_2 \) by the Fenton reaction (Fig. 7). We plotted \( \text{H}_2\text{O}_2 \) and Fe\(^{2+}\) evolution
as predicted by the model for a set of different values of pyrite reactive surface area (in Fig. 7a). As a result of this coupling effect, higher values of reactive surface area tend to increase the amount of secondary ROS (i.e., OH·/O−, HO2·/O2·−, O2) rather than stabilize the presence of H2O2 in solution (in Fig. 7b)2,48.

Discussion
Aqueous suspensions of pyrite form H2O2, in the presence and absence of dissolved O2, following a generation-decay trend (Fig. 1). The asymmetric shape observed in the experimental curves indicated that the apparent rate of H2O2 generation was significantly faster than the apparent H2O2 degradation. Previous studies22,25
have suggested that in the presence of dissolved O₂, pyrite slurries form H₂O₂ by an electron transfer between the ferrous iron defect sites (Fe²⁺ − S) and the adsorbed O₂ through a Haber–Weiss reaction, involving the O₂− radical formation (equations 1 and 2). This hypothesis is consistent with the observation that there is an inverse relationship between H₂O₂ and O₂ at the beginning of the oxic experiment (Fig. 2a). The mechanism of H₂O₂ formation in anoxic conditions remains more controversial. Some studies have suggested that in absence of O₂, the formation of H₂O₂ is driven by the oxidation of adsorbed H₂O catalyzed by the pyrite surface⁴,¹⁹,²³,²⁶, whereas other studies have considered that this reaction is unlikely due to energetic considerations⁴⁵,⁵⁵. A possible reconciliation comes from considering the presence of Fe³⁺ dangling bonds generated from the cleavage of S–S bonds. Briefly, the rupture of S–S bonds generate S− species which are highly instable and, to compensate its charge disequilibrium, donate one electron to the nearest iron atom by the autoredox reaction²⁶,³¹,³²,⁴⁹–⁵⁴.

\[ \equiv S^- + \equiv Fe^{2+} \rightarrow \equiv S^{2-} + \equiv Fe^{3+} \]  (10)

These dangling bonds could decrease the energy requirements for the chemisorption of H₂O molecules, some authors even talk about “ferryl” iron dangling bonds \( \equiv Fe^{4+} \cdot \), leading to H₂O splitting into H⁺ and OH⁻, with the subsequent formation of H₂O₂, as described by equations 3 and 4. Our experiments showed that H₂O₂ was generated in the absence of both dissolved O₂ and light (Fig. 1b). Besides, the estimated ratio of S/Fe (≤2) in unreacted pyrite particles (Supplementary Fig. S8) indicated the presence of S vacancies.

Experiments with pyrite slurries under both oxic and anoxic conditions showed a sudden drop of pH during the first hours (Supplementary Fig. S2). This increase of H⁺ concentration together with the progressive accumulation of H₂O₂ and Fe²⁺ in solution is expected to trigger the Fenton reaction. UV-Vis spectroscopy confirmed the presence of Fe³⁺-complexes during anoxic pyrite dissolution (Fig. 3a) whose maximum wavelengths were compatible with the following reaction⁴¹:

\[ Fe_2(OH)_2^+ (\lambda_{max} = 340nm) + SO_4^{2−} (\lambda_{max} = 430nm) + H^+ = Fe_2(OH)(SO_4)^{3+} \]  (11)

The detection of both Fe³⁺-complexes and OH⁻ in solution (Fig. 3) indicated that the Fenton reaction occurred even in the absence of dissolved O₂, supporting the idea that the suite of Fenton reactions conditioned the decay period of H₂O₂ curves. Additionally, the formation of OH⁻ concomitantly with the formation of H₂O₂ from the start-up of the experiment under anoxic conditions (Fig. 3b) together with the splitting of the cathodic peak associated with the nearly spontaneous iron reduction (Supplementary Fig. S3), suggest that \( \equiv Fe^{3+} \) dangling bonds, actually catalyze the H₂O oxidation by one single electron, forming OH⁻ as described by equation 3.

In principle, the overall process of aqueous pyrite oxidation -under oxic conditions- involves only O₂(ż) consumption, according to:

\[ FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2−} + 2H^+ \]  (12)

However, considering a free radical mechanism, a simultaneous uptake and release of dissolved O₂ it to be expected, because it can be both a product and a reactant. In oxic experiments, O₂ concentration rapidly dropped and then reached a more constant value at these early stages, the consumption of O₂ during this period could be attributed to Fe²⁺-oxidation at surface sites to form the superoxide anion (O₂⁻) and to the subsequent production of H₂O₂ (equations 1 and 2). An interesting result was the formation of O₃(μγ) as a by-product in anoxic experiments (Fig. 2b and Supplementary Fig. S1b). Although O₃ is not a direct product in the equation 3, since H₂O₂ is formed, the formation of O₃ can occur via several pathways such as the Fenton-like reaction, the "catalase-like reaction" or via non-radical disproportionation of H₂O₂.

XPS and HRTEM results reported herein showed the formation of Fe³⁺−O patches over pyrite surfaces. The implication of these Fe³⁺−O patches during aqueous pyrite oxidation is not clear. Some studies argued that the electron cycling of Fe³⁺ and Fe²⁺ between unoxidized and oxidized areas favors the electron transfer from the surface of the pyrite to molecular O₂, increasing the oxidation rate of pyrite⁴⁶. However, this mechanism is based on atmospheric oxidation of pyrite and does not explain the formation of H₂O₂. In contrast, other studies have suggested that the formation of these Fe³⁺−O patches interrupts the redox cycling of Fe³⁺/Fe²⁺, thereby inhibiting the formation of H₂O₂ and decreasing the rate of pyrite dissolution⁴⁵. Our cycling experiments showed that most of the defect sites of the pyrite microparticles remained active at the end of the experiment, even when H₂O₂ was no longer observable in solution (Fig. 4). Moreover, it is expected that oxidized patches will desorb at low pH during the pyrite dissolution process. HRTEM images showed an appreciable increment of the pyrite alteration layer (Supplementary Fig. S9), suggesting that these Fe³⁺−O patches failed to completely block the surface renewal during pyrite dissolution.

Based on our experimental results, we propose a model that explains the generation-decay trend of H₂O₂ in terms of a kinetic competition between (1) the formation of H₂O₂ by the self-oxidation of iron–sulfur cluster defect sites; and, (2) the degradation of H₂O₂ by the Fenton reaction triggered by pyrite dissolution. Accordingly, the evolution of H₂O₂ in solution can be summarized as follows:

\[ \frac{d[H_2O_2]}{dt} = \sum \frac{d[H_2O_2]_{surf}}{dt} + \sum \frac{d[H_2O_2]_{Fenton}}{dt} \]  (13)

At the beginning of the model run (t≈0), the amount of H₂O₂ in solution was controlled by the surface reaction and the second term tended toward zero. However, when the Fenton reaction started, H₂O₂ was progressively degraded to secondary ROS, in solution (i.e., OH⁻, HO₂⁻, O₂). At the end of the model run the amount of H₂O₂ remained constant within a value close to zero and equation 13, became:
The model allowed us to estimate the rate constants of $\text{H}_2\text{O}_2$ formation under both oxic and anoxic conditions (Table 1). Peak production of $\text{H}_2\text{O}_2$ was shifted towards longer times in anoxic conditions (Supplementary Fig. S10), pointing to slower oxidation kinetics of pyrite in the absence of $\text{O}_2$, a result also supported by our XPS analysis (Supplementary Figs S4 and S5) and by the sulfate and iron released by pyrite dissolution (Supplementary Fig. S11). When compared with experimental data, the model reproduces qualitatively well the observed trends for $\text{pH}$, $\text{O}_2$, $\text{Fe}^{2+}$, and $\text{SO}_4^{2-}$, as these parameters are calculated using the overall equations of pyrite dissolution$^{17,21,28}$ (Fig. 6a–b). An additional feature of the model is that provides a way to reconcile the classical dissolution approach with the free radical assumption, opening a new pathway to analyze the flux of secondary ROS resulting from the degradation of $\text{H}_2\text{O}_2$, through the Fenton reaction (Fig. 6c–d). OH· radicals were the first species produced, rapidly decaying to $\text{HO}_2$·. These ROS species counterbalances the decrease in pH and promoted the so-called "Fenton like" reaction, which resulted in the formation of $\text{O}_2(g)$. $\text{Fe}^{3+}$ regenerated through this sequence, and also through the dissolution of pyrite, makes the Fenton reaction more efficient$^{29}$. Therefore, the disappearance of $\text{H}_2\text{O}_2$ in solution was likely due to a fast transformation into ROS, catalyzed by dissolved $\text{Fe}^{3+}$, rather than by the cessation of the generation mechanism itself. This result is consistent with the continuous production of $\text{H}_2\text{O}_2$ and $\text{OH}^{-}$ during pyrite dissolution. We hypothesize that as a result of the progressive acidification of the solution together with iron recycling by the Fenton reaction, the abiotic dissolution of pyrite microparticles can be considered as a natural and auto-catalytic Fenton reagent, useful to understanding long-term oxidation processes even in oxygen limited environments.

**Methods**

**Sample preparation and characterization.** Natural pyrite samples (Logroño, Spain) were ground to obtain particles with average diameter of 1.4 μm, Laser Diffraction Particle Size Analyzer (LS13320) and BET (Brunauer – Emmett – Teller) surface area of 1.46 m$^2$/g (multi-point $\text{N}_2$ adsorption). Prior to use, freshly solved $\text{O}_2$ were measured using UV-vis spectroscopy by monitoring absorption bands at specific wavelengths. To obtain particles with average diameter of 1.4 μm, Laser Diffraction Particle Size Analyzer (LS13320) and BET (Brunauer – Emmett – Teller) surface area of 1.46 m$^2$/g (multi-point $\text{N}_2$ adsorption). Prior to use, freshly solved $\text{O}_2$ were measured using UV-vis spectroscopy by monitoring absorption bands at specific wavelengths. To prevent data masking due to particle absorption, the pyrite microparticles were washed by sonication in ethanol (96%) and hydrochloric acid (HCl 0.25 M), to remove organics and oxide surface coatings. Samples were then rinsed with deoxygenated deionized water (MilliQ) and dried in a low vacuum chamber purged with nitrogen ($\text{N}_2$) until used. Minor and trace elements in the acid washed samples were evaluated by scanning electron microscopy (SEM) using X-ray mapping (XRM) (Supplementary Fig. S8). X-ray diffraction (XRD) was used to assess the presence of secondary phases and to characterize the degree of structural disorder in the samples using the Rietveld method (Supplementary Fig. S12).

**Batch kinetic experiments.** The kinetics of $\text{H}_2\text{O}_2$ formation and degradation on pyrite slurries was investigated in batch reactors utilizing amperometric sensors for $\text{H}_2\text{O}_2$ (ISO-HPO-100, World Precision Instruments, Inc.) and dissolved $\text{O}_2$ (Unisens DK), and a glass electrode for pH determination (Vernier FPH-BTA). Batch reactors were designed to fit with microsensors, spectroscopic probes, ports for pyrite inlet under $\text{N}_2$ atmosphere, and valves. The valves allowed fluid circulation and solution sampling in a closed system configuration.

The production of ferric iron ($\text{Fe}^{3+}$) and hydroxyl radical (OH·) species by pyrite slurries in absence of dissolved $\text{O}_2$ were measured using UV-vis spectroscopy by monitoring absorption bands at specific wavelengths. To prevent data masking due to particle absorption, the pyrite microparticles were washed by sonication in ethanol (96%) and hydrochloric acid (HCl 0.25 M), to remove organics and oxide surface coatings. Samples were then rinsed with deoxygenated deionized water (MilliQ) and dried in a low vacuum chamber purged with nitrogen ($\text{N}_2$) until used. Minor and trace elements in the acid washed samples were evaluated by scanning electron microscopy (SEM) using X-ray mapping (XRM) (Supplementary Fig. S8). X-ray diffraction (XRD) was used to assess the presence of secondary phases and to characterize the degree of structural disorder in the samples using the Rietveld method (Supplementary Fig. S12).

**Surface analysis.** Cyclic Voltammetry (CV) was employed as an additional way to assess the sequence of redox reactions involving free radicals during $\text{H}_2\text{O}_2$ adsorption at pyrite interface. CV was performed using Pt/Pyrite-Nps/Naion®/electrodes in $\text{N}_2$ purged solutions vs Ag/Cl 3 M KCl. A detailed description of the experimental set-up is given as Supplementary Material. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface oxidation states of (001) faces of pyrite (single-crystal, ~1 cm$^2$ × 2 mm) after aqueous reaction in oxic and anoxic conditions. Platelets parallel to (001) faces were cut (1 cm$^2$ × 2 mm) after aqueous reaction in oxic and anoxic conditions. Platelets parallel to (001) faces were cut (1 cm$^2$ × 2 mm) and cleaned following the same procedure described above and allowed to react with water in oxic and anoxic conditions. Samples were dried and stored in $\text{N}_2$-filled tubes until introduction into the XPS vacuum chamber. The oxidation states were analyzed at three different stages of the dissolution process: (t$_{s}$) unreacted sample; the pyrite crystal was acid-washed to generate oxide-free surfaces by removing the normal contaminants, carbon, nitrogen, and oxygen (C, N, O) due to atmospheric oxidation; (t$_{s}$); sample after 22 hours immersed in oxic water. (t$_{s}$); sample after 22 hours immersed in anoxic water. Prior to this stepped analysis, the XPS spectra of a pyrite surface was analyzed after argon ion ($\text{Ar}^{+}$) sputtering to verify the formation of $\text{Fe}^{3+}$ and $\text{S}^{2-}$ surface species as occurs during mechanical fracture by preferential sulfur removal. XPS Spectra were collected from a take-off angle of 90° relative to the sample surface in a Thermo Scientific K-Alpha ESCA analyzer using monochromatic Al K$_\alpha$ (1486.6 eV) radiation and pass energies of 100 eV and 20 eV for survey spectra and narrow region spectra, respectively. Spectra were aligned by setting the C1s peak to a binding energy of 285 eV$^{18}$. Deconvolution and fitting of experimental data were done.
with the XPSpeak4.2 software (http://www.phy.cuhk.edu.hk/~surface/XPSPEAK/). The Shirley method was used for background subtraction and the binding energies of the species identified were assigned using values taken from literature (Supplementary Tables S2 and S3).

High resolution Electron Transmission Microscopy (HTREM) analysis were performed to identify nano-domains of secondary oxidation products at the pyrite interface. HTREM images were acquired on a JEOL JEM-3011 microscope with accelerating voltage of 200 kV using a Gatan Ultrascan 1000 CCD camera and Digital Micrograph software. Data processing was performed with the GADDS and image-J codes. Pyrite lamellas were prepared using a focused ion beam (FIB) with a high resolution JEOL JSM-6700 f.

**Kinetic model.** The model was run using the computer code Copasi 4.8 (COmplex PAthway Simulator)\(^2\). We assume that the experimental trend of H\(_2\)O\(_2\) in the presence and absence of O\(_2\) (g) is shaped by three main processes: (i) the rate of H\(_2\)O\(_2\) generation by the iron defect sites on the surface of pyrite particles; (ii) the production rates of Fe\(^{2+}\) and SO\(_4^{2-}\) by pyrite dissolution; and, (iii) the kinetics of H\(_2\)O\(_2\) degradation by the Fenton reaction. Fits to the experimental curves that describe the evolution of H\(_2\)O\(_2\) were performed using the Marquardt algorithm employing as adjustable parameters the rate constants of the H\(_2\)O\(_2\) formation. A detailed explanation of the modeling set-up is included in the supplementary material.

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Author Contributions

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All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar
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