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Unravel the rate of pyrite oxidation under weathering conditions: An experimental approach

Julien POOT, Alexandre FELTEN, Julien COLAUX, Guillaume LEPECHEUR, Pierre LOUETTE, Augustin DEKONINCK & Johan YANS

Context and objectives

Pyrite is one of the most common sulfides on Earth. It occurs in many geological settings, in sedimentary rocks and hydrothermal deposits, including polymetallic sulfides ore deposits. The oxidation of pyrite can lead to environmental issues due to **acid mine drainage** (AMD, Fig. 1) but also extraction difficulties requiring specific mining processes [1,2].

For the experimental approach, many pyrite samples (Fig. 2) were collected from the Hautrage Clay Formation (Late Barremian to earliest Aptian; Mons Basin, Belgium). In these clayey rocks, pyrite has remained protected from atmospheric conditions and can be considered as **fresh**. The objective is to determine the oxidation rate of pyrite by different experiments : (I) **open air exposure**, (ii) **underwater**, (iii) **drip exposure** to tridistilled water. **XPS** (X-Ray Photoelectron Spectroscopy, Figs 2,3) analyses are carried out at different time steps on the surface and at depth of the samples to decipher the extend of the **oxidation zone** (more than 6,000 hours of experiment). pH measurements are also carried out for underwater pyrite to detect oxidation (Fig. 4), which is much more discrete than the air and drip exposure pyrite.



Fig. 1 - Example of Acid Mine Drainage (AMD); Lousal inactive Mine (Portugal).

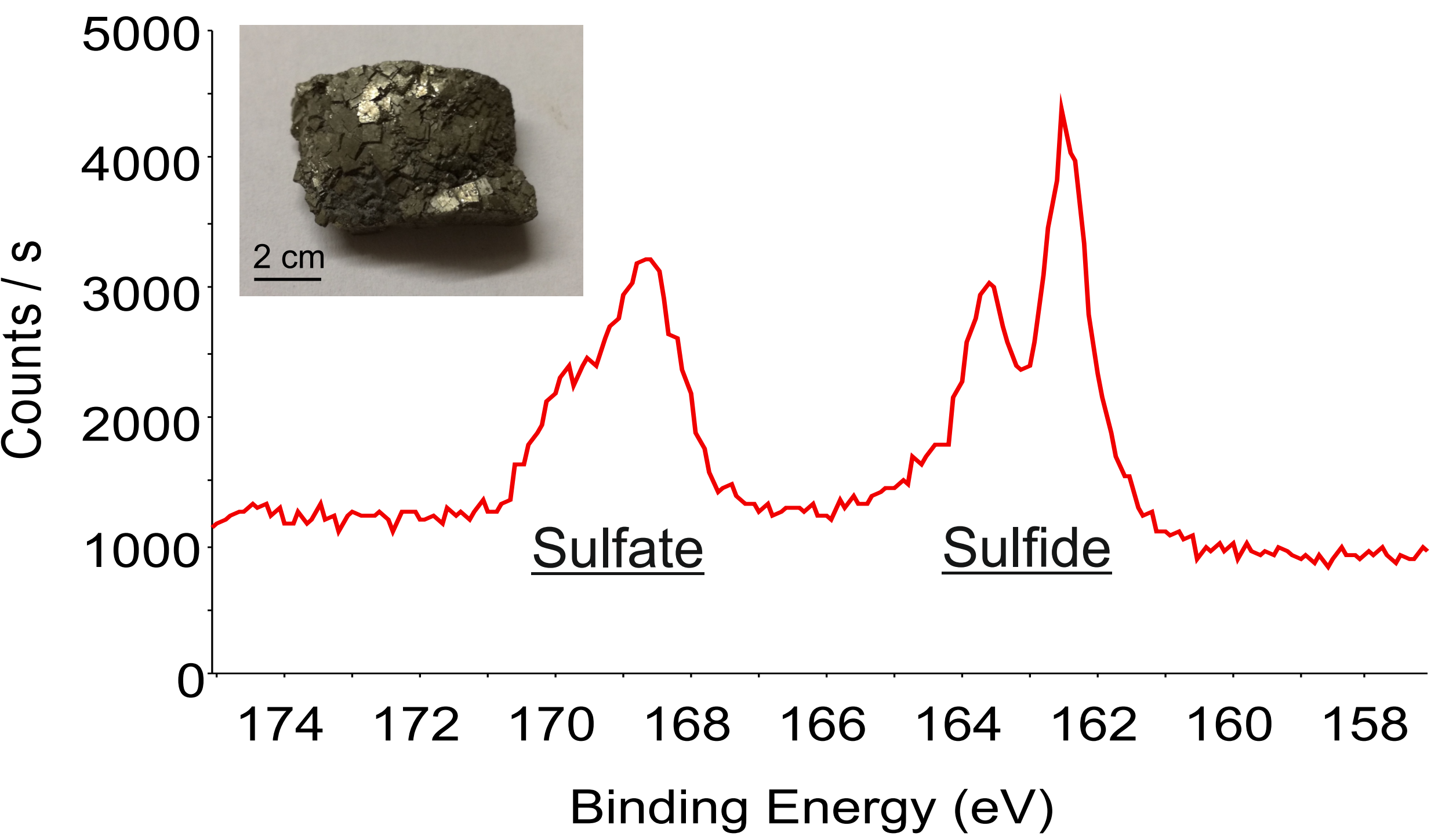


Fig. 2 - X-Ray Photoelectron Spectrometry (XPS) typical survey for sulfur scan (S2p).

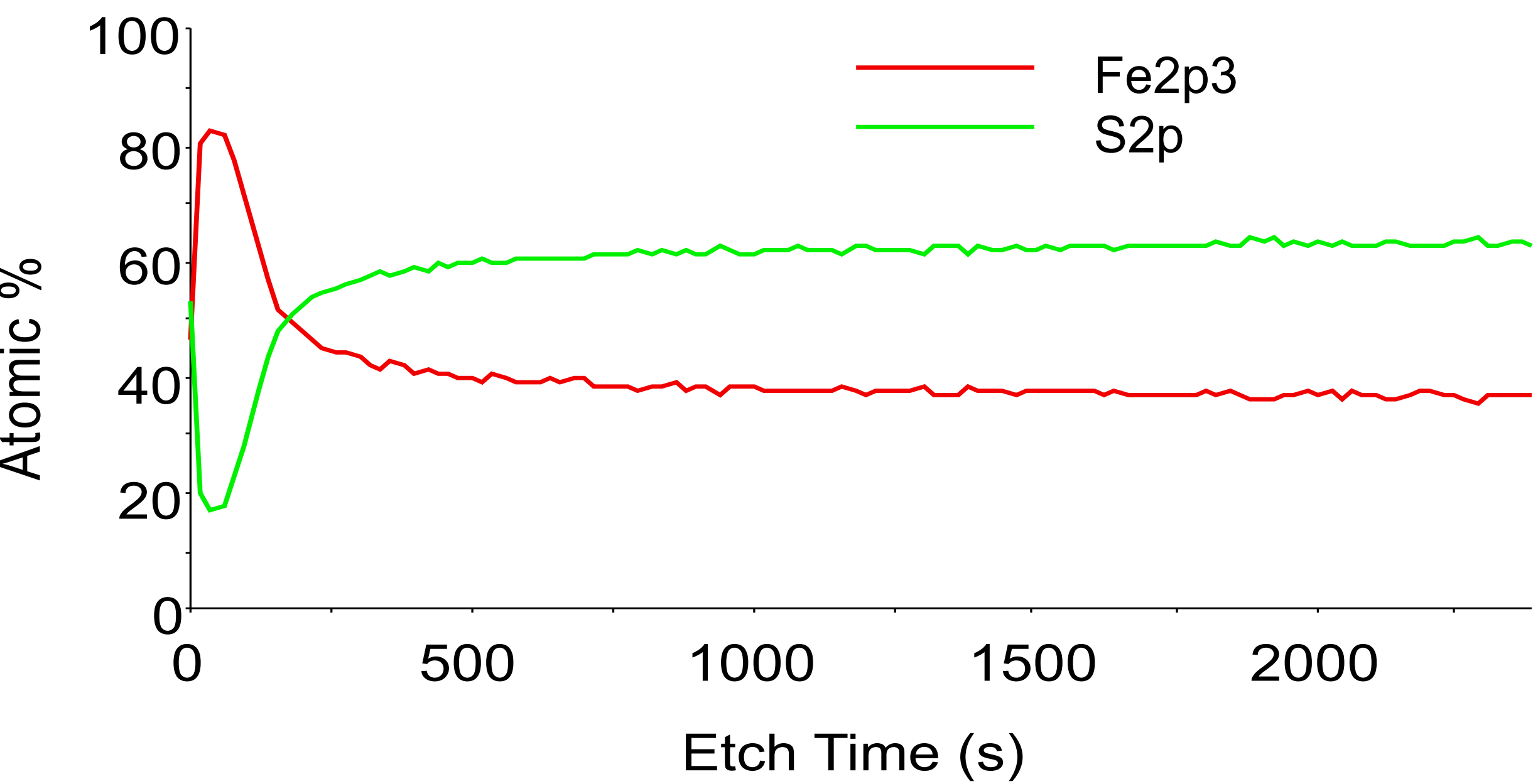


Fig. 3 - Atomic profile for iron (Fe2p3) and sulfur (S2p) using XPS peaks data.

Conclusions

At a human scale, this oxidation depth seems to be low but can be responsible for many **environmental** (aquatic life or aquifers) and **construction-related issues** (stability, cracks in walls, heaved floors, ...) that could take place over decades. Figure 6 shows a typical example of heaved floor in pyrite-bearing shales.

At a geological time scale, tens of thousands years (~ one meter per million year) would be sufficient to fully oxidize the pyrite (Fig. 7) then form secondary minerals and thus supergene profiles.



Fig. 6 - Example of heaved floor at Johnson City Public Library (USA) [3].



Fig. 7 - Example of oxidized pyrite from the Agoujgal deposit in Morocco

Results and hypotheses

The first results show an estimated **oxidation depth of 0.85 micrometer** for drip exposure pyrite over a **6 months period**. This value is initially (few hundred hours) twice as low for air exposure pyrite but quickly becomes much lower than the drip exposure one (Fig. 5). Underwater pyrite shows slight oxidation which is mostly observed by pH measurements (lab temperature between 20 and 25°C, Fig. 4). Even if the depth of oxidation is only a few tens of nanometers, the pH decreases quickly until it “stabilizes” at a pH of ~2. This experiment is mainly carried out to highlight the acidity of meteoric fluids but also the role of clays in the **neutralization process**.

The difference of oxidation depths for the different experiments can be explained by different factors. On the first hand, there is the **leaching** which will have a crucial role in the release of **sulfates**, minerals generally observed on the surface of air exposure pyrite during XPS analyses. This leaching allows a deeper oxidation observed for drip exposure pyrite where iron oxides are observed. On the other hand, when there is no leaching, sulfate can act as a protective layer and slow down the oxidation at depth. Moreover, the crystalline form of the pyrite could also impact the oxidation. Whether cubic or not, diagenetic or hydrothermal, even microfractures can facilitate the penetration of distilled water and so impact the depth of oxidation. For underwater pyrite, limited oxidation is due to the the stability of (secondary) sulfides at sample scale. Once the oxygen has been consumed, a sufficiently reductive environment can be established in the vicinity of the pyrite surface thus limiting the oxidation

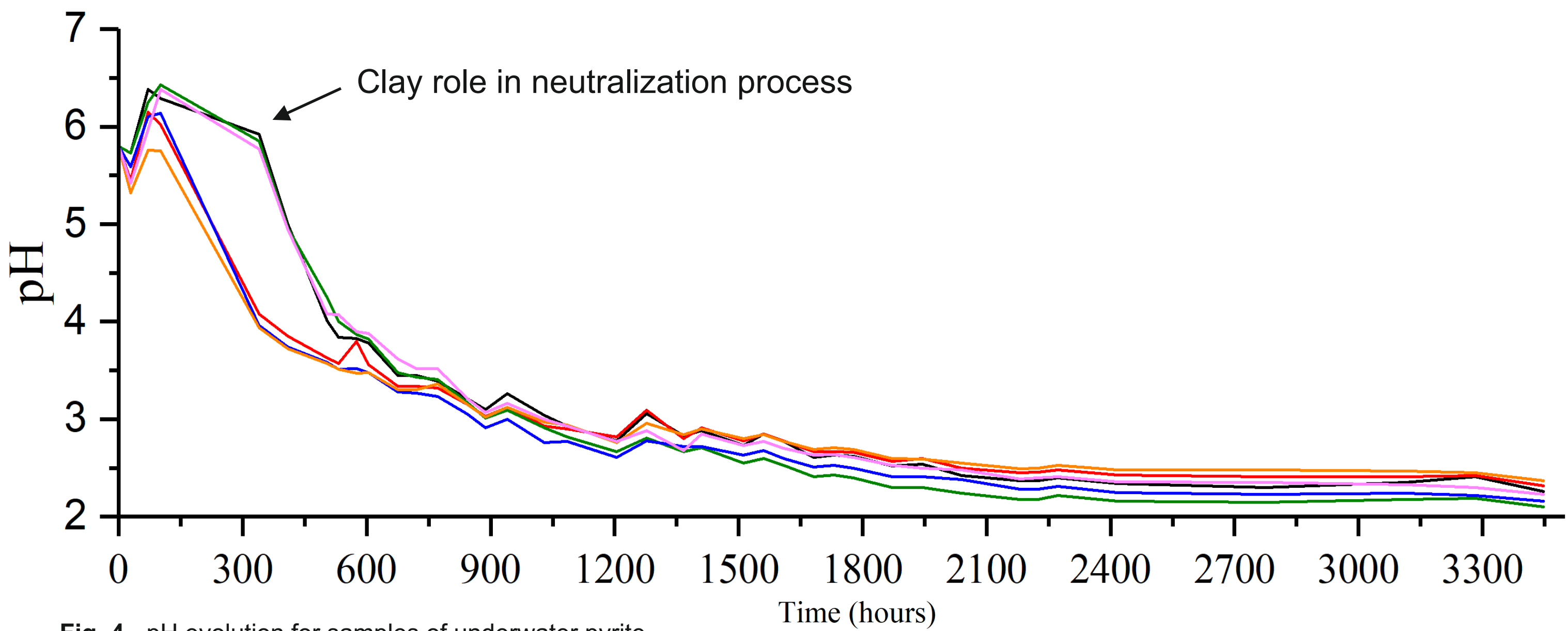


Fig. 4 - pH evolution for samples of underwater pyrite.

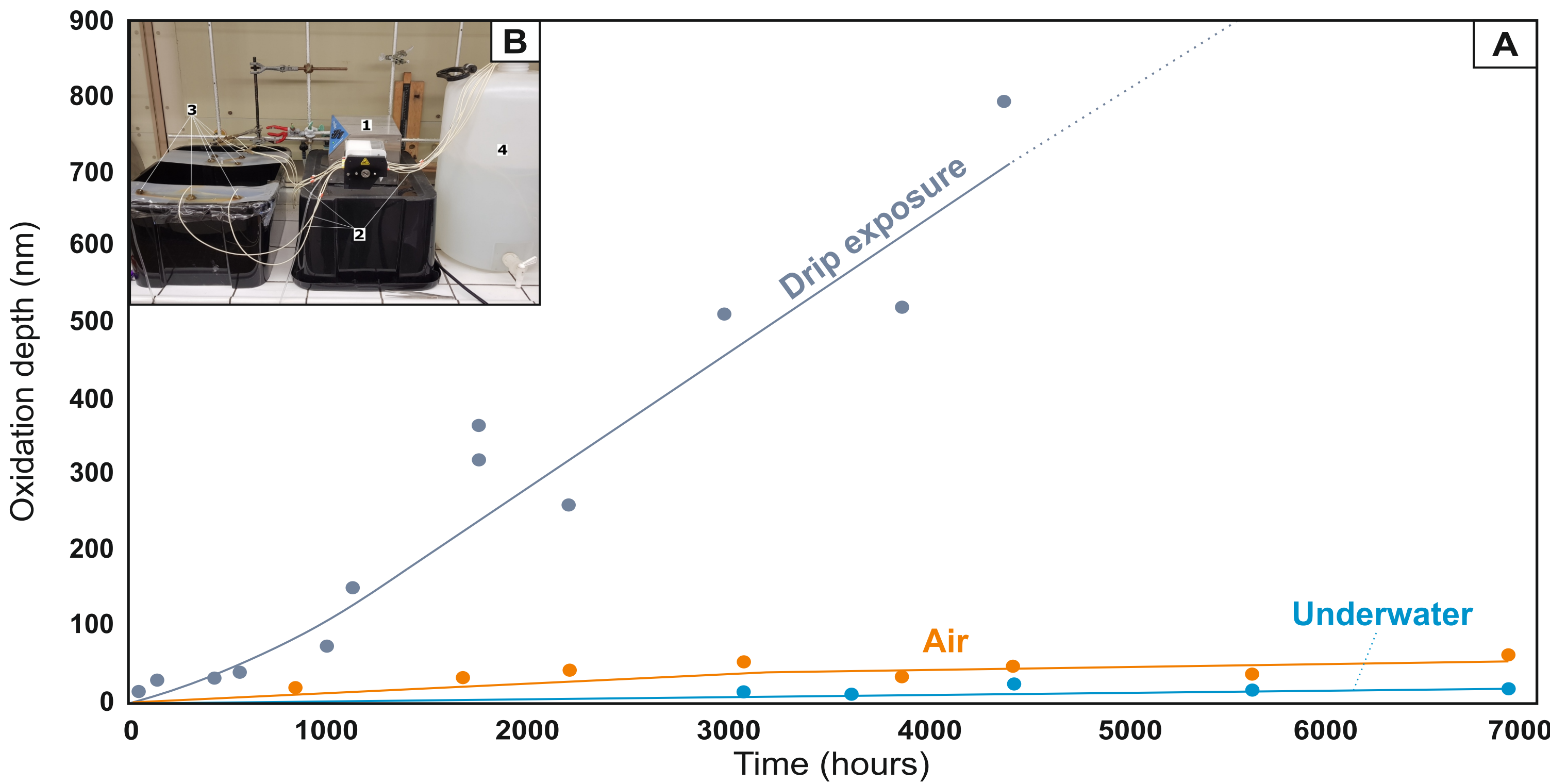


Fig. 5 - (A) Evolution of oxidation depth for air, underwater and drip exposure pyrite. (B) Experimental system: Pump (1) with polypropylene tubes (2) with tridistilled dripping water (4) on pyrite (3).

References

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