

REACTIVE OXYGEN SPECIES FORMATION WITH PYRITE UNDER ANOXIC CONDITIONS

Melike Balk, Mariette Wolthers, Aleksandra Galic, Paul Mason (Utrecht University, the Netherlands) and Husn Ubayda Islam (University College London and ESRF DUBBLE)

The question of how free oxygen became available on the early Earth is still shrouded in uncertainty. We have studied processes that result in oxygen formation during simple weathering in an initially anoxic subsurface environment. Reactive Oxygen Species (ROS) are precursors to molecular oxygen during this process. Due to their toxicity they may have strongly influenced the evolution of early life. A possible way out of this dilemma comes from a study for the formation of ROS on the early Earth is iron sulfides such as pyrite. We hypothesized that this source of ROS on the early Earth provided a significant electron sink that influenced the metabolic pathways of evolving microorganisms. We proposed to exploit the XANES technique to detect changes in $\text{Fe}^{2+} / \text{Fe}^{3+}$ and in Fe mineralogy over the course of our experiments at the surfaces of iron sulfide materials.

We developed an experimental set-up that was modified and extended from our previous study (DUBBLE, 26-01-986). In the new experimental set-up, we examined iron speciation on the surfaces of reactants and products from the experiments in order to better identify the reaction pathways that result in the pyrite breakdown. We investigated anoxic pyrite oxidation across a wide temperature- and pH-range. We also managed to perform a long-term pyrite experiment at ambient temperature.

Oxidized species were thoroughly purged from pyrite surfaces through acid-washing and oven-drying following the methods in the literature. We have tested either dry pyrite or pyrite with miliQ-water under anoxic conditions. Crushed, grained, and sieved anoxic pyrite samples were mixed with silica by using a mortar to promote even dispersion in solutions or in dry forms. The mixtures were loaded in to capillary tubes of 2 mm and sealed under anoxic conditions in an anaerobic bag. Then, samples including dry pyrite controls were incubated for several hours at different time- and temperature- (between 20 to 70 °C) intervals before acquisition of XAS spectra and compared to several standard solids and solutions. To examine the role of ROS on pyrite, we designed a set of anoxic pH buffered (pH=2, 3, 5, 7, 10) solutions with pyrite.

The results showed that the environment of Fe^{2+} at the pyrite surface varied considerably depending on experimental time and conditions, e.g. temperature, pH. As an example in Figure 1, the XANES of the pyrite in miliQ-water shows that aqueous ferrous iron was produced in the end of the reaction at ambient temperature. However, mixture of Fe-forms was observed at the pyrite surface, such as surface Fe coordinated to H_2O_2 and SO_4 besides S_2 . Additionally, the accumulation of Fe^{2+} and the formation of ROS might likely cause Fenton's reaction to proceed. We observed that pH had also an effect on the reaction. Below pH 4, the pyrite surface contained the above-mentioned mixture of Fe^{2+} environments. As the pH was raised, less contribution of iron-oxygen species was observed.

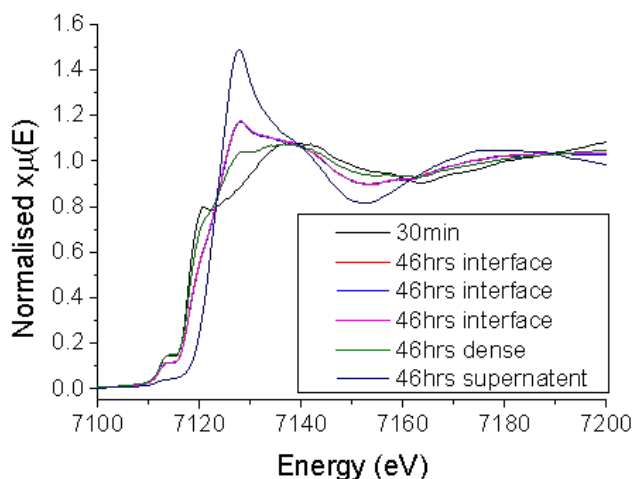


Figure 1. XAS spectra of pyrite in miliQ-water after the prolonged-incubation of room temperature.