REACTIVE OXYGEN SPECIES FORMATION WITH PYRITE UNDER ANOXIC CONDITIONS

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We proposed to examine iron speciation on the surfaces of reactants and products from our experiments in order to better identify the reaction pathways that result in the pyrite breakdown. This required a detailed study of the corresponding formation of oxygenating radicals and changes in iron speciation both in solution and at mineral surfaces. We aimed to relate our findings with the oxygen evolution theories during the earliest history of the Earth.

Oxidized species were thoroughly purged from pyrite surfaces through acid-washing and oven-drying following the methods in the literature. We have tested pyrite with the combination of deionized water, sea water and Mars solution under anoxic conditions. Crushed, grained, and sieved anoxic pyrite samples were mixed with PVP (Polyvinylpyrolidone) by using a mortar to promote even dispersion in solutions. The mixtures were loaded in to capillary tubes of 2 mm and sealed under anoxic conditions. Then, samples including dry pyrite controls were incubated for four hours at three different temperatures, room temperature, 45°C to 70°C before acquisition of XAS spectra and compared to several standard solids and solutions.

The results showed a chemical oxidation sequence. As an example in Figure 1, the XANES of the pyrite in miliQ-water shows significant variation from solid pyrite and similarities to $FeSO_4$ solution. Most possibly, some surface ferrous iron was oxidized to ferric iron, which subsequently oxidized some sulfide to sulfate. Fenton's reaction cannot be excluded as an additional pathway. Therefore, we observed a change in oxidation state from Fe(II) to a mixture of Fe(III) and Fe(II) and possibly variations in oxygen-atom association with iron. It was not a complete conversion to Fe(III). We observed that temperature had also a positive effect on the reaction. Our data achieved will contribute to our understanding of the kinetics associated with these reactions.

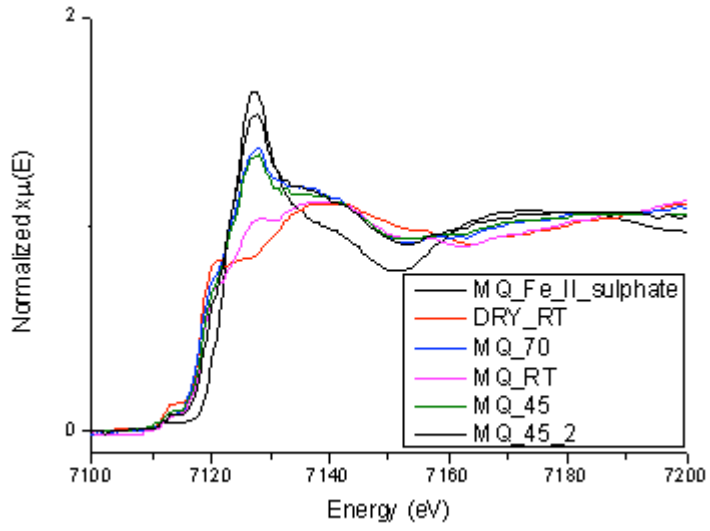

Figure 1. XAS spectra of pyrite in miliQ-water after the incubation of room temperature (RT), 45°C and 70°C, compared with dry pyrite and Fe(II)sulphate.