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LES SCIENCES DE LA CONSERVATION DU PATRIMOINE ET LE DÉVELOPPEMENT DURABLE
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The influence of oxygen content and relative humidity on pyrite decay

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Introduction

Pyrite is formed with contribution of bacteria in sedimentary rocks containing organic residues. It can be found e.g. in coal, bituminous limestones, claystones and others as a very common fossilization mineral.
In the presence of oxygen and air humidity, pyrite oxides according to the following chemical reaction:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ FeSO_4 + 2\ H_2SO_4$$

At the same time, the oxidation of ferrous ions to ferric ions may occur and various minerals may form, such as limonite, goethite and hematite. Some products of decay further increase the rate of decay, as they are often hygroscopic, form hydrates or attack the surrounding matter.
Pyrite decay is one of the most serious problems when caring for the mineralogical and paleontological collections. It is generally acknowledged that the rate of decay is influenced by many factors, such as relative humidity, bacterial activity or presence of oxygen and other chemical substances. To prevent the decay, it is important to identify the relevance of each of these factors and to determine the most detrimental ones and – hopefully – the most easily controllable in the long term time frame. This work examines the influence of oxygen content and of relative humidity on pyrite decay.

Experiment

Three types of samples were used for the purposes of the experiment: pyrite monocrystals (2x2x2 cm, Navajun, Spain), clusters of pyrite crystals (up to 5 mm, San Jose de Huanzala Mine, Peru) and clusters of marcasite crystals (up to 5 mm, Bílina, Czech Republic). Two series of samples were prepared. Both series of samples were placed in sealed boxes with RH 11-97% controlled by the presence of saturated salt solutions. In case of the second series, the oxygen content was increased by the presence of hydrogen peroxide solution (30%). This modification slightly increased the relative humidity above the value usually obtained by the presence of saturated salt solution. This increase is a result of the dynamic equilibrium between the evaporation of hydrogen peroxide solution and the effect of saturated salt solution.

Results and discussion

It was found that the presence of increased oxygen content has significant effect on pyrite decay. After 48 hours of exposition, droplets of slightly yellowish solution were found on the surface of the pyrite cube exposed to RH = 97% with increased oxygen content. The solution was identified as sulphuric acid with iron (III) sulphate content (Fig. 1). In case of pyrite and marcasite clusters, no sign of decay was visible after 48 hours. This may be caused by the soaking of formed acid into the pores and crevices that are present on crystals surfaces, while in case of intact monocrystal the acid can freely flow down the surface.
After one week, the signs of decay were observed in case of all samples exposed in environment with increased oxygen content while in case of samples with unmodified oxygen content there were no signs of decay.
After three months of exposition, still only samples exposed in environment with increased oxygen content showed signs of decay (Fig. 2). The appearance of degradation products changes with increasing relative humidity of the atmosphere. At RH = 30%, only thin layer of fine greyish crystals is visible. At RH ranging from 45 to 70%, the volume of crystals increases significantly and the colour of crystallites changes from white to yellow. At RH = 70%, droplets of sulphuric acid solution are visible at the bottom of the pyrite cube. At RH = 97%, droplets of sulphuric acid are visible in case of all samples.
Samples exposed in atmospheres with various relative humidity and normal oxygen content did not show any signs of decay even after 6 months of exposition.

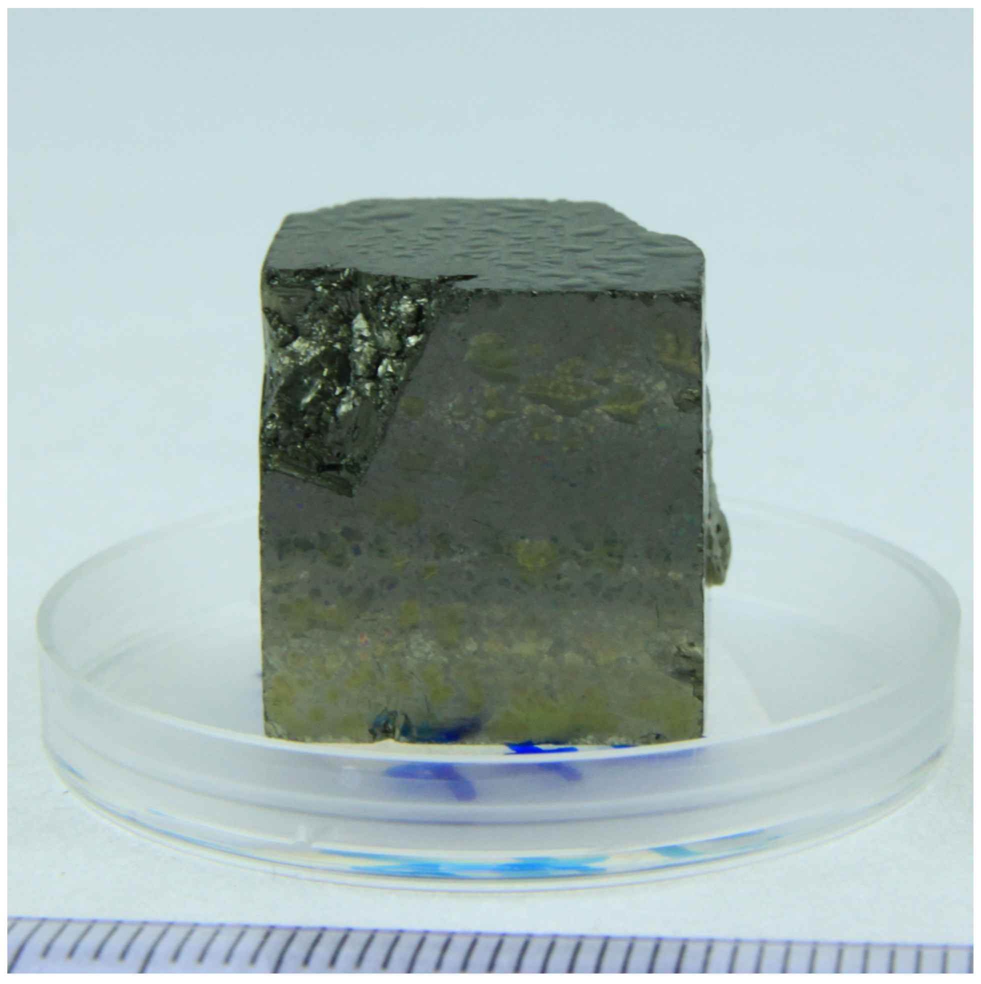

Fig. 1. Pyrite cube exposed for 48 hours in atmosphere with RH = 97% and increased oxygen content. Droplets of sulphuric acid solution are visible on the surface of the cube.

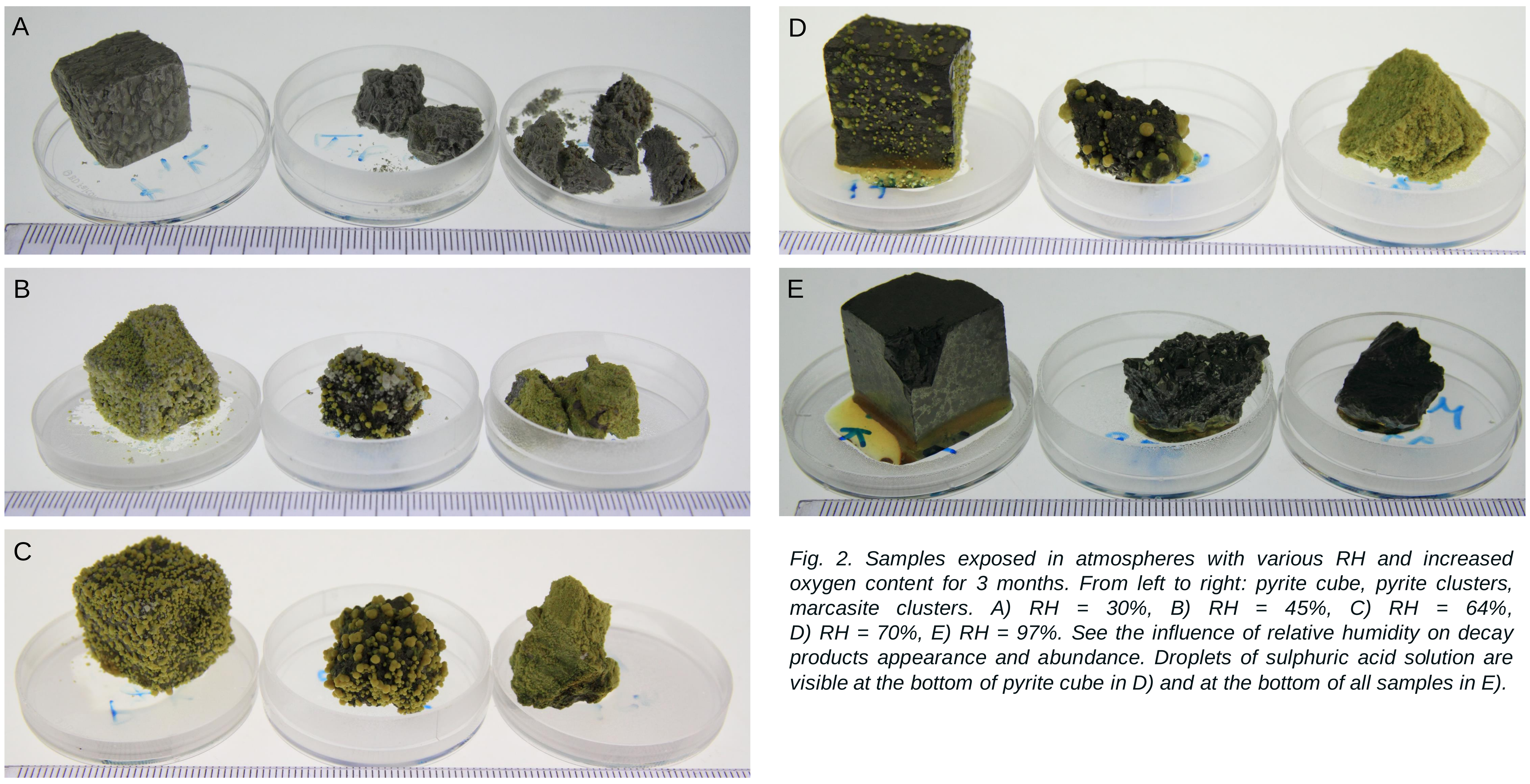

Fig. 2. Samples exposed in atmospheres with various RH and increased oxygen content for 3 months. From left to right: pyrite cube, pyrite clusters, marcasite clusters. A) RH = 30%, B) RH = 45%, C) RH = 64%, D) RH = 70%, E) RH = 97%. See the influence of relative humidity on decay products appearance and abundance. Droplets of sulphuric acid solution are visible at the bottom of pyrite cube in D) and at the bottom of all samples in E).

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