NatSCA supports open access publication as part of its mission is to promote and support natural science collections. NatSCA uses the Creative Commons Attribution License (CCAL) http://creativecommons.org/licenses/by/2.5/ for all works we publish. Under CCAL authors retain ownership of the copyright for their article, but authors allow anyone to download, reuse, reprint, modify, distribute, and/or copy articles in NatSCA publications, so long as the original authors and source are cited.
Pyrite Decay: cause and effect, prevention and cure.

Nigel R. Larkin

The Natural History Department, Norfolk Museums and Archaeology Service, Shirehall, Market Avenue, Norwich, Norfolk NR1 3JQ, UK.

Email: nrlarkin@easynet.co.uk

Abstract

Pyrite (FeS$_2$) is a common mineral found in igneous, sedimentary and metamorphic rocks; it may be present in petrology, mineral and palaeontological collections. Pyrite decay, or pyrite oxidation, has been recorded since the 19th century and various methods have been devised over the years to prevent or ‘cure’ it with varying degrees of success. Methods of identifying pyrite decay in collections are discussed along with potential problems this can cause to the specimens and associated labels. Up to date prevention methods are discussed, including microclimates, controlled environments, collections surveys and resin coatings. Modern techniques of ‘curing’ pyrite are discussed in detail, including ammonium gas treatment and Ethanolamine Thioglycollate treatment.

Introduction

Exactly ten years ago the Natural Sciences Conservation Group provided a day-long seminar about pyrite decay at the Natural History Museum in London, consisting of talks and demonstrations. It might be useful to repeat this event or something similar every five or ten years as there will always be some people new to the profession to whom the issue is a mystery, and some who would like a refresher - particularly as the subject has a long history of confusion over the exact nature of the processes involved. An example of a late 19th century response to pyrite decay describes how “the preparators mistakenly believed that the Pyrite disease was caused by an unknown germ and developed a method to counteract its effects... The bones were soaked in a mixture of alcohol, arsenic and shellac.... The alcohol was able to penetrate the bones, carrying the arsenic (supposed to kill the mysterious “germ” causing the problem), and the shellac successfully hardened the weaker parts” (Spalding, 1993).

Shinya and Bergwall (2007) recently provided a concise summary of what pyrite is, how it decays and (briefly) how specimens may be treated, but their PDF poster included only some of the practical ways of preventing - or at least reducing the likelihood of - pyrite decay. Some other important preventive measures are described below, along with relevant notes about the nature of pyrite and how it decays.

What is pyrite?

Pyrite (FeS$_2$), also known as ‘fools gold’, is a common mineral found in sedimentary, metamorphic, and igneous rocks. It grows in crystalline forms, typically cubic or octahedral. The crystal can be several centimetres in diameter for well-grown cubes, or microcrystalline (Howie, 1992). It can occur either compact, well crystallized and stable or porous, microcrystalline, often impure and very unstable. Marcasite (FeS$_2$) is a dimorph of pyrite that primarily occurs in sedimentary rocks. It is not as commonly found as pyrite but it too can be unstable and susceptible to oxidation (Rixon, 1976; Cornish, 1987; Shinya & Bergwall, 2007).

Mineral and palaeontological specimens that consist almost wholly of pyrite are easily identified as such, as they look and feel ‘metallic’. It is much less easy to identify those specimens that contain a relatively small amount of pyrite (where it is finely disseminated through the specimen), or in which the pyrite has developed only within the inner pore spaces of what was once bone, for example.

How does pyrite ‘decay’?

Pyrite oxidation (also known as pyrite ‘disease’, pyrite ‘rot’ and pyrite ‘decay’) is caused and accelerated by the presence of oxygen and water, even in relative humidities (RH) as low as 60%. Only a few days exposure to an inappropriate humidity may be enough for the decay process to be triggered in some specimens (for more information on the factors controlling the rate of pyrite decay, see Newman (1998)).
When oxidation of pyrite is triggered, the following chemical process happens over time:

\[(4\text{FeS}_2 + 13\text{O}_2 + 2\text{H}_2\text{O}) \gg (4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + 2\text{SO}_2)\]

(pyrite, oxygen, water) \gg (ferrous sulphate, sulphuric acid, sulphur dioxide)

It appears that some pyrite oxidation may be caused by or be related to the bacteria *Thiobacillus ferrooxidans* (Temple & Colmer, 1951) and *Thiobacillus sp* (Beijerinck, 1904) - reclassified recently as *Acidithio-bacillus ferrooxidans* and *Acidithiobacillus* respectively (Kelly and Wood, 2000). However, this interaction typically occurs above 95% humidity (Howie, 1992; Butler, 1994) and therefore should not be an issue in most museum collections. The bacteria may be merely opportunistic, or possibly just catalytic, arriving after the reaction has started (Leiggi & May, 1994).

A specimen suffering from pyrite oxidation is often easily identified. Usually it will have lost some surface shine, the surface will develop a crust of white and/or yellow crystals (Figs. 1 & 2), it will begin to smell sulphurous and it may show signs of cracking. Associated labels may exhibit ‘scorch marks’ (Fig 3). The exact nature of the by-products of the oxidation process will depend on the mineral composition of the fossil and matrix associated with the oxidizing pyrite or marcasite, but are generally sulphuric acid and various hydrated sulphates (e.g., ferrous sulphate, copiapite, fibroferrite or melanterite) (Wang et. al., 1992; Shinya & Bergwall, 2007). Although the symptoms of advanced pyrite oxidation can look terrible at first and specimens can be completely destroyed, it is often the case that careful cleaning and appropriate remedial treatment may save a specimen. The ammonite in Figure 2 looks like it has to be thrown away, but after careful cleaning with a brush followed by some consolidation and gluing it is still a useable specimen (Fig. 3).
Quite apart from being unsightly and potentially a health hazard the dry, powdery sulphuric acid and/or hydrated sulphates can be quite deleterious for a specimen. If not seen and dealt with in a timely fashion not only can the whole fossil be destroyed but also the accompanying labels or cards identifying the specimen that has been lost. The storage media – card trays, wooden boxes etc – can also be destroyed in the process, including the base of a wooden drawer and even the specimens in a drawer beneath. This is one of the reasons people used to think it was a ‘disease’ that could spread. In all these instances the sulphuric acid is attacking the cellulose present in the paper, card or wood.

Fig. 2. A small fossilised Jurassic ammonite (approximately 40 mm diameter), preserved partly in pyrite. It has suffered from pyrite oxidation, as evidenced by the mass of grey powder covering it. This dry sulphuric acid or hydrated sulphate has damaged both the specimen and the label, leaving both much weaker and friable. The label states that the specimen has been treated before for pyrite decay, but no details were noted on the label and the specimen has continued to deteriorate – possibly because the storage conditions did not change if the specimen was returned to the same place after treatment. This shows the importance of improving the storage conditions for a specimen after cleaning and/or treatment (i.e. by lowering the RH).

Fig. 3. The same ammonite as in Figure 2 after cleaning and repair.
Importantly, as well as being corrosive the oxidation product is several times the volume of the original mineral. Because pyrite is often present deep inside a specimen the resulting crystal growth and expansion can cause the specimen to fracture (Fig. 4), crumble, and slowly shatter - sometimes catastrophically. Framed and glazed specimens on display that have succumbed to pyrite decay have been known to expand so much that the specimen has pressed against the (non-safety) glazing and forced it to bow outwards. If not detected in time, this could lead to a violent shattering of the glass in a public exhibition space (Cornish et al., 1995; Rajan, 1995).

Fig. 4. A fragment (approximately 60 mm across) of a nodule of radiating pyrite after significant pyrite decay. There are two symptoms of pyrite decay in evidence: the white crystalline powder on the internal face to the right of the image, and the deep cracks in the external surface of the specimen, on the left of the image, where sections of the external surface have pulled away from one another as the specimen has expanded.

Another reason that the oxidation process was thought to be a disease was because in collections arranged stratigraphically or geographically, many fossils from the same site or area would be stored together. These would naturally often contain roughly the same amount and type of pyrite so that when the environmental conditions were right, the oxidation of the pyrite in several specimens would begin more or less around the same time. The cabinets would be opened many months or years later to reveal dozens of specimens decaying beneath corrosive yellow and gray powder.
Testing for pyrite oxidation
Pyrite oxidation, especially in the early stages, is not always obvious (Fig 5), so any yellowish or grey powdery crust should be investigated. If a specimen is suspected to be suffering from pyrite oxidation but the outwards signs are minimal, two simple tests can be applied. One is to press Universal Indicator paper moistened with distilled water against the area of a specimen thought to be affected. This will confirm whether the pH is less than, more than or equal to 3, and therefore if it is acidic (indicating by-products of pyrite decay are present) or not (Cornish & Doyle, 1984; Andrew, 1999). The other test is to moisten a small area of a specimen with little ammonium hydroxide. On drying, this will turn brick red if the by-products of pyrite oxidation are present (Rixon, 1976).

Pyrite affecting Labels
The paper specimen label in Figure 3 has been ‘burnt’ by the by-products of decay. It is not just discolouration, the paper affected can become extremely fragile and friable and corrodes away eventually if the powder is not removed. Such a label is still acidic and should be replaced. To remove the acidic products from pyrite decay, labels should be treated (see below) or washed in water (Stooshnov & Buttler, 2001) and kept stored in a polyester sleeve.

Prevention: climates and microclimates
The damage that pyrite oxidation inflicts on a specimen is irreversible. Therefore although the by-products can be dealt with and the oxidation process arrested and neutralized (see below), it is better by far to prevent the oxidation of pyrite in the first place. Moisture and oxygen are the two factors leading to pyrite decay.

Fig. 5. Pyrite oxidation on the surface of a break in a large pliosaur vertebra. The by-products can be seen in the centre of the picture as a greyish mass in the middle and a yellow crust in the centre and around the edges of the affected area. The scale bar is 50 mm long.
Completely eliminating both can be achieved, but at great cost and inconvenience so a compromise inevitably has to be reached. Maintaining a low enough humidity in a storage area will either prevent the oxidation of the pyrite being triggered, or it will slow down the reaction if it is already underway. RH should preferably be about 30%, but more realistically 45% should be aimed for and certainly always less than 60% (Howie, 1992). Unfortunately, although the environment of some stores may be perfectly controllable, many stores are not so easily controlled and other types of material may be present that require higher levels of RH to maintain their own integrity and stability.

If the RH of a storage environment is not easily controlled and if specific specimens in that area are known to be susceptible to pyrite oxidation, many specimens can easily be housed permanently within the collection in individual suitable storage media to provide appropriate microclimates. They can be sealed within laminate films that exclude moisture and oxygen (even whole cupboards can be sealed this way), or in desiccation chambers made of Perspex or similar material. Oxygen scavengers can be placed within these media for further protection. A cheaper and easier alternative for many specimens is to use a suitable lidded polyethylene or polypropylene container (they are usually impervious to moisture and oxygen), with a desiccant placed inside along with the specimen(s). Desiccants work either by absorption or adsorption of atmospheric humidity. The most common types of desiccants are silica gel, a molecular sieve or preconditioned Artsorb (a moisture-sensitive silica material providing over five times the moisture buffering capacity of regular density silica gel). The ensuing RH of the sealed microclimate can be monitored with a colour-changing card also placed within the container. Useful large lidded polypropylene containers are available (for instance ‘Stewart Boxes’ up to 320 mm x 320 mm wide by 160 mm deep), but the quality of the container is of paramount importance as it’s seal must close effectively (Larkin et al, 1998). Also, it is important to take their lids off immediately if they are bought with the lids attached, so that the volatile organic compounds from the manufacturing process can off-gas rather than be trapped (Larkin et al, 2000).

**Prevention: maintaining buildings**

Much effort can be expended attempting to control RH within a storage area with dehumidifiers etc but this is for nothing if the building housing the geology collection is not maintained properly: gutters, downpipes and storm drains should be checked regularly, especially during and after building work. It may take only one incident to trigger the process of oxidation. Two specific examples follow.

Kate Andrew (1999) reported that the severe pyrite decay affecting the large marine reptiles on display at Whitby Museum was due to several problems caused by poor building maintenance. These related to guttering and down pipes, and also leaking skylights. The symptoms of this inadequate maintenance included saturated walls, algal growth on exterior walls and salt efflorescence on interior walls. In one display case a completely dissolved and re-crystallized specimen of sylvite provided independent evidence that relative humidity in that case had reached over 85%. Thermohygrograph charts from the previous winter had recorded relative humidity rising to 76% in the gallery. The roof rainwater collecting system was found to be blocked by, amongst other items, dead birds, a football and a training shoe. Monitoring of the moisture content of the wall suggested that rising damp may also have been a problem.

At the Natural History Museum in London a collection of over a hundred Jurassic marine reptile skeletons are on permanent display on the wall of a long gallery leading to the Palaeontology Department. Many of these specimens are important historically and/or scientifically, including several specimens collected by Mary Anning. Unfortunately, during building work in the early 1990s the rainwater drainage system behind the wall was damaged and to make matters worse this was not realized for some time. A three-year conservation project ensued to remedially conserve, neutralize and clean dozens of specimens (some very large) that had suffered from pyrite oxidation as a result (Cornish et al 1995; Rajan, 1995).

**Prevention: collection surveys**

Time and money spent trying to reduce the RH levels in a collections area to lower the chances of pyritic specimens oxidizing is wasted if there is no material susceptible or if there is only a small amount of pyritic material that could easily be stored in appropriate media with a more controlled microclimate. The trick is to know which specimens, if any, in a collection should be isolated and stored in a controlled low RH microclimate. There are two approaches, and both should be applied. Firstly, there is some information in published literature as to what specimens have deteriorated badly in the past, and from which stratigraphic horizons and/or geographical localities. For instance, fossils from the Liassic, Gault and London Clay are prone to the problem (Rixon, 1976), including ammonites and marine reptiles from the Liassic strata of Dorset. Specimens in mineral collections are of course at risk as well, including pyrite, chalcopyrite and marcasite.
Secondly, undertaking a manual (rather than desktop) survey of a collection to identify high risk areas is worthwhile. An experienced person would know which sub-collections to prioritise, but ideally every single drawer, box or cabinet in a geology collection would be given a visual inspection to locate pyrite-rich specimens and check if there are any pyrite issues currently requiring remedial measures. A list of specimens ‘at risk’ could then be created and ideally these specimens would be checked every year or so. For larger collections, a rolling programme of checking one section of the collection each year in turn may be more practical.

**Prevention: resin coatings**

Applied directly to a specimen, consolidants and varnishes etc were once used to prevent air from coming in contact with the specimen’s surface. Unfortunately, such coatings varied greatly and are mostly not impermeable to air and humidity (Cornish & Doyle, 1984). Some resins can provide some limited buffering by decreasing a specimen’s natural porosity (Costagliola et al, 1997) and in that way slightly reduce their ability to be affected by moisture. However, treatment in this manner adulterates a specimen and ultimately will be detrimental to further analytical or conservation processes and is not recommended considering the possible beneficial effects are only slight (Buttler, 1994).

**Moulding and casting**

If important specimens (e.g. type and/or figured) are considered to be susceptible to pyrite decay, it is worth making good quality moulds of them to produce replicas in case the originals are damaged by pyrite oxidation in the future. Good quality rubber or latex should be used, and the cast should be made soon after moulding as the rubber or latex mould will degrade over time. Ideally, both the mould and cast should be accessioned and labelled. Interestingly, natural latex rubber contains ammonia as a preservative so its use as a moulding material can have the added benefit of neutralizing to some extent any sulphuric acid and ferrous sulphate present. Although not tested in a controlled scientific experiment, it has been reported that this method was successful in halting the oxidation process in some specimens (Shinya & Bergwall, 2007).

**Cure**

Once it has started the oxidation process cannot be reversed but there are two reliable ways to treat specimens to neutralise the sulphuric acid and remove the by-products. Both are a little technical and require some equipment and chemicals. The following descriptions of these processes are only summaries (after Shinya & Bergwall, 2007) and the relevant references should be consulted for detailed instructions and health and safety guidelines.

**Cure: Ammonium gas treatment**

Ammonium gas has been successfully used to neutralize sulphuric acid in specimens affected by pyrite decay (Bannister, 1933; Bannister and Sweet, 1943; Rixon, 1976; Birker and Kaylor, 1986; Howie, 1992; Waller, 1987; Andrew, 1999). Specimens are suspended above a solution of ammonium hydroxide and enclosed by polyethylene or glass to contain the gas created by evaporation. The RH above the solution can reach 70% unless mixed with polyethylene glycol (PEG) in a 10% (volume to weight) solution. This will provide a RH of about 30%. Because porous pyrite will absorb water vapour (resulting in further oxidation) it is important that the ammonium solution be made with a non-aqueous solvent.

Method:
1. Make 10% volume to weight solution of ammonium hydroxide in polyethylene glycol (PEG).
2. Place a plastic coated metal rack over the solution and place specimen on top.
3. Cover the apparatus with polyethylene or glass to treat the specimen with ammonium vapour.
4. Treatment is complete when white or yellowish patches on specimen change to rust coloured stains.
5. Clean the specimen with alcohol and thoroughly dry.

This technique is particularly useful for neutralising small specimens, very friable specimens and specimen labels that have been affected by pyrite decay. Unfortunately, it is a very difficult procedure to apply to large specimens or those still on display that are attached to a wall, especially if in a public area. However, it is not impossible. Andrew (1999) describes using this technique on large specimens in a geology gallery with the rest of the museum still open to the public, utilising a temporary conservation lab with walls made of heavy duty polyethylene sheeting fixed with wooden batons. Local extraction was achieved using a Nederman fan and trunking to vent outside via a window or under-floor vent. However, in such cases health and safety regulations may now pose significant problems as ammonia is both toxic and flammable.
Cure: Ethanolamine Thioglycollate treatment
Ethanolamine thioglycollate both neutralizes sulphuric acid and removes oxidation by-products, perhaps more effectively than ammonium gas treatment. Ethanolamine thioglycollate is an alkaline liquid that is soluble in both ethanol and isopropanol, hence the specimen being treated will not be exposed to water. Before treatment as much of the by-products of oxidation should be removed as possible with soft brushes or an air-abrasive unit, to expose the specimen surface (Cornish and Doyle, 1984; Cornish, 1987).

Method 1: Immersion in solution
1. Make a 2% to 5% ethanolamine thioglycollate solution in ethanol or isopropanol.
2. Immerse the specimen in solution for between one and four hours. Change the solution when it becomes a dark violet colour, otherwise brown insoluble precipitation will stain the specimen.
3. Wash specimen with alcohol.
4. Repeat the process until the solution no longer changes its colour when specimen is immersed.

There are some problems with this method. Old consolidants and glues etc will probably be dissolved by the solution which would risk a consolidated or glued specimen falling apart. It is not a very useful method for large specimens or those remaining on display, especially large marine reptiles attached to a gallery wall. Also, specimens can remain stained, labels will be stained and some old iron-based inks may dissolve, both those applied to labels and those applied directly to the specimen. It is therefore wise to photograph all specimens and labels before treatment.

Method 2: Paste application
1. Make a 3% to 5% ethanolamine thioglycollate solution in ethanol or isopropanol.
2. Mix equal amounts (1:1 ratio) of the solution and sepiolite (magnesium silicate).
3. Apply the paste to the affected area and cover it with polythene or aluminium foil to prevent rapid evaporation.
4. Leave specimen covered for between 1- and 3 hours.
5. Clean and wash the specimen or treated area with alcohol.

Although not as fully effective as the immersion technique above, the paste is useful for friable specimens that would disintegrate with immersion (though for very friable specimens the ammonia gas treatment would be better). The paste application is also useful for specimens that have been heavily consolidated previously. It is also useful for specimens too large to immerse and for specimens on display, particularly for those mounted vertically on a wall (Andrew, 1999).

It is important to remember that although all these treatments will arrest the pyrite decay and neutralise its deleterious effects, the treated specimen will remain susceptible to further oxidation. Indeed, further decay is likely if the specimen is returned to the same storage environment in which the oxidation process was triggered rather than stored permanently in a manner that will provide an appropriate regime of relative humidity.

Acknowledgements
The author would like to thank Steve McLean who extended an invitation to deliver a talk on pyrite decay at the NatSCA AGM in Newcastle in 2011. Thanks also to the anonymous reviewer who provided very useful comments.

References


