PYRITE OXIDATION AND MUSEUM COLLECTIONS: A REVIEW OF THEORY AND CONSERVATION TREATMENTS.

by Andrew Newman



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The literature relating to the causes of pyrite oxidation is extensive and widely dispersed, and the conclusions drawn often appear contradictory. Different mechanisms for the oxidation process are advocated, many of which are supported by experimental evidence that is difficult to evaluate. The range of literature relating to the problem of pyrite oxidation in a museum context is more limited and has resulted in a consensus about conservation treatments, although these have yet to be proven successful in the long term. This review will build upon the earlier critiques published by Howie (1977a, b, 1992) and Waller (1987) and consider the most recently published work. The review is necessarily selective concentrating on the literature which has significance to museum collections.

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Introduction

Howie (1977a, 1992) stated that the oxidation of pyritic specimens in museum collections is one of the most potentially damaging conservation problems encountered by curators and conservators of geological material. However the problem is not confined to geological specimens, vulnerable specimens may be contained within a range of collections For example, Oddy (1977), described problems caused by pyrite oxidation in archaeological collections.

The oxidation process and its consequences are recognisable by the presence of a white, yellow or greenish efflorescence, often accompanied by deep cracks in the specimen (see Figures 1 & 2). There is always a sulfurous smell present. It appears as if the specimen is being forced apart internally which results in its fabric or form being distorted. The products of the oxidation reaction are acidic and are capable of damaging associated labels and storage furniture (see Figure 2).

In order to reduce damage to specimens, to minimise further damage to affected specimens and to determine a conservation strategy, it is important to have a clear understanding of the current knowledge of the mechanisms of pyrite oxidation and the factors which influence reactions and their rates.

Possible mechanisms for the chemical oxidation of pyrite

A number of different mechanisms, either acting independently or in conjunction with each other, have been proposed for pyrite oxidation over recent years. These are a) molecular, b) bacteriological and c) electrochemical. Experimental work has also indicated that a number of factors will influence the rate of the reaction. The relationship between the reaction, its rate and any subsequent damage to specimens in a museum environment will be discussed later in this article.

Waller (1987), Howie (1992) and Lowson (1982) described a broad based oxidation process which results in a variety of ferrous-ferric-sulfate-hydroxide-hydrate phases and sulfuric acid. Waller (1987) gave the predominate overall reaction at high RH as:

2FeS2+702+n+m2H20 \rightarrow 2FeS04•nH20+2H2S04+mH20

Also at low and moderate RH and 25C the following reaction is quoted.

FeS2+H2O+302→ FeSO4•H2+SO2

Both the oxidation products are hydrated and the sulfuric acid is in solution in water. It is important to note that the hygroscopic nature of the oxidation products have the potential to facilitate the reaction by the absorption of water.

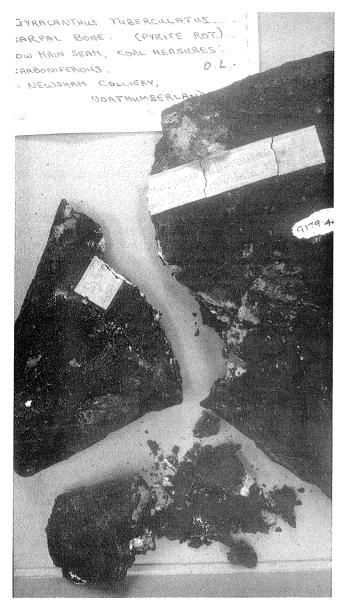


Figure 1. *Gyracanthus tubercalatus* bone. NEWHM: G179.44. Before treatment.

Smith and Shumate (1970) and Pugh, Hossner and Dixon (1984) after practical studies presented a case for two reaction pathways for oxidation, firstly, one which involved chemical activity alone and secondly, a path which consisted of the oxidation by ferric ions which are formed from ferrous ions by bacteria. Nordstrom (1982) also makes a clear distinction between organic and inorganic mechanisms. The possible role of bacteria in relation to the rate of reaction is discussed later in this article.

An electrochemical mechanism was discussed by Howie (1986a, 1992), Peters (1984), Bang (1994) Luther (1987) and Lowson (1982). Howie (1992) stated that it might "contribute as much as 50% of the oxidation mechanism". This may explain the apparent susceptibility of specimens which are associated with carbon (Bang 1994). This vulnerability was demonstrated by Howie (1979b) who showed experimentally that "the carbonaceous pyritic specimens



Figure 2. Fossil wood. NEWHM: G149.42. Before treatment. Note damage to label.

showed a tendency for some oxidation to occur below 50% RH". Bang (1994) stated that the reason why framboidal pyrite (Rust 1935; Wilkin and Barnes 1997; Schopf, Ehlers, Stiles and Birle 1965; Love 1958) when associated with organic matrices was very susceptible was that each framboidal spheroid reacts like a galvanic system when moisture enters it by capillary action. It was concluded that in this system pyrite is oxidised anodically creating acidic conditions which lead to the chemical and mechanical breakdown of the framboidal pyrite spheroids. This interesting theory does not account for the loss of specimens which are not associated with carbon. The above work has lead to the possibility of new treatments using plasma-ashing methods (Hollahan and Bell 1974; Bang 1994) to remove the carbon from specimens, so disrupting the electrochemical process. This technique will be discussed later in this article.

The literature does not provide a consensus view as to which of the above mechanisms controls the oxidation process. It is probable, however, that all of the mechanisms discussed play a role in particular environments. However, the fundamental driving force of pyrite oxidation remains unclear despite many years of study.

Factors controlling the rate of pyrite oxidation

The reviews by Howie (1992), Waller (1987), Nordstrom (1982) and Lowson (1982) as well as the experimental work by Morth and Smith (1966) Smith and Shumate (1970) and Khawaja (1975) concluded that the oxidation reaction, its rate and subsequent

damage to specimens was probably dependent on a number of factors. These are the surface area, availability of water, temperature, pH, bacteria and oxygen concentration, in an aqueous or gaseous state. The role of trace element distribution was discussed by Caruccio (1972).

Surface area

Experimental work by Howie (1979b, 1992), Pugh, Hossner and Dixon (1982) Smith and Shumate (1970) and Khawaja (1975) indicated that the surface area of the pyrite influenced the rate of the oxidation reaction. These authors stated that microcrystalline or framboidal pyrite (Rust 1935; Schopf, Ehlers, Stiles and Birle 1965; Love 1958; Wilkin and Barnes 1997) is more reactive than massive, due to the available surface area upon which the reaction can occur. The study published by Howie (1979b) showed that compact pyrite had "little tendency to absorb moisture and oxidise even at high RH during the test period", which was 105 days. He stated that specimens with "microcrystalline and framboidal pyrite showed a wide variation in their capacity to oxidise". Pugh, Hossner and Dixon (1984) reported that "a two fold increase in reaction rate occurs for the frambroidal pyrite compared with the massive". Khawaja (1975) from the basis of an extensive study showed that it was possible to classify pyrite by its rate of oxidation. Every sample of highly oxidisable pyrite studied had a grain size of less than 10 microns with associated carbon, moderately oxidisable pyrite had a grain size in the 15-25 micron range, with little associated carbon and pyrite that was weakly oxidisable, had a grain size of over 25 microns with no associated carbon. Curracio (1972) described a study carried out on the stability of pyrite in relation to mine drainage. He stated that "size alone is not the answer, coarse grained pyrite was mechanically ground to 0.5 microns and after 3 weeks the ground sample was still yellow and bright and showed no signs of decomposition". If this work is accurate it appears to indicate that the relationship between surface area and reactivity may not be direct in all cases. Lowson (1982) also stated that the published experimental data is not really sufficient to support a clear link. The possibility that framboidal pyrite may play an important role in an electrochemical mechanism for oxidation (Bang 1994) has been mentioned earlier.

The role of water

Morth and Smith (1966) quoted a study carried out by Kim (1964) which showed that that over a limited temperature range the rate of the oxidation reaction varied in a linear fashion with absolute humidity of water in the vapour phase, suggesting that water was a reactant. Studies by Morth and Smith (1966) and Smith and Shumate (1970) showed that the oxidation rate increased steadily as a function of RH. They also

suggested that the role of water may be to dissolve the oxidation products from the pyrite surface, which would otherwise inhibit the oxidation reaction on a dry surface. Studies carried out by Waller (1989) showed that oxidation rates increased exponentially as RH increases from 10% to about 60%. Water is also significant in that it enables ferrous sulfate, a product of the oxidation reaction to hydrate at an RH of about 60% (Waller 1987) which results in a molar expansion. The importance of this process to the stability of museum collections is discussed later in this article.

Temperature

Waller (1987), Morth and Smith (1966) and Smith and Shumate (1970) showed the relationship between temperature and the oxidation rate. This was represented graphically by Morth and Smith (1966) and Smith and Shumate (1970). These results showed clearly that the reaction proceeded more quickly with an increase in temperature. The authors calculated that the oxidation rate will approximately double for each 10°C rise in temperature at a constant RH.

pH

Waller (1987), Howie (1992) and Smith and Shumate (1970) discussed the role of pH on the rate of the reaction. Howie (1992) stated that under alkaline conditions oxidation products can build up on the reactive surface of the pyrite and slow the rate of the reaction. Waller (1987) stated that there is little or no dependency of the oxidation rate on pH over the range -1<pH<4 and at higher levels the oxidation rate will increase as a function of pH. Smith and Shumate (1970) showed experimentally that as the pH increased the oxidation rate increased rapidly. They were not able to explain these results as conventional wisdom would suggest the opposite would be true (Howie 1992). Nordstrom (1982) stated that in aqueous environments below a pH of 3 the oxidation rates are independent of pH and above 4 rate limiting steps, described in the paper, are pH dependant.

Oxygen concentration

Morth and Smith (1966) and Smith and Shumate (1970) showed experimentally that if the oxygen concentration in water surrounding the reactive site on the pyrite increased the rate of the reaction also increased. They also stated that the presence of nitrogen gas reduces the rate of oxidation. Waller (1987) did not deal with this subject in detail but mentions oxygen concentration as a possible factor controlling oxidation rates.

Sulfur reducing bacteria

The possible role of sulfur reducing bacteria in effecting the oxidation reaction has been considered by Pugh, Hossner and Dixon (1984) in lignite specimens and Siverman (1967) in pyrite concentrates from coals. Nordstrom (1982) and Smith and Shumate (1970) also proposed a mechanism for oxidation involving bacteria.

Pugh, Hossner and Dixon (1984) described a number of studies (Temple and Koehler 1954; Lorenz and Tarpley 1963; and Wilson and Zuberer 1976) which considered the role of bacteria such as *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* on the oxidation rate of various iron sulphides as well as carrying out their own experimental work. They noted that the results of these studies were very variable and other factors must play a role. However, they concluded that the presence of *Thiobacillus ferriooxidans* can "significantly increase pyrite oxidation".

Silverman (1967) described a practical study from which he concluded that two methods of bacterial oxidation of pyrite occur. Firstly a method which required physical contact between bacteria and pyrite particles for biological pyrite oxidation. The second is an indirect method which involves "bacteria oxidising ferrous ions to the ferric state thereby regenerating the ferric ions required for chemical oxidation of pyrite." Smith and Shumate (1970) also described a direct and indirect method of biological oxidation. They also showed that sulfur reducing bacteria require a high RH to operate.

Trace elements

The possibility that trace element distribution may play a role in the oxidation reaction and subsequent stability of pyrite was discussed by Caruccio (1972). In his study 18 samples of pyrite were analysed, these included both reactive and inert samples. The results showed that there was more titanium in the stable samples than in the reactive ones and silver was present in the reactive samples and absent from the stable ones. Caruccio asked the question whether titanium stabilises pyrite or silver causes pyrite oxidation, however, Smith and Shumate (1970) stated that trace elements and other metals were not a major factor influencing reactivity.

Discussion of pyrite oxidation mechanisms and factors influencing the rate of reaction in relation to museum specimens.

As can be seen from the selective review given above, the literature concerning pyrite oxidation and factors controlling its rate is extensive and to some extent contradictory. The original impetus for research on pyrite oxidation related to its possible involvement in explosions in coal mines and more recently in relation to acid mine drainage water, a source of environmental pollution. Despite the bias of the research to mining problems it is possible to apply much of the consequent

results to the museum situation and use the data to draw conclusions as to the safest environmental parameters in which to store vulnerable pyritic specimens.

The different mechanisms and reaction pathways proposed for pyrite oxidation are important because if they are applicable to a museum environment they will influence conservation strategies.

The fact that increased temperatures speed up the oxidation reaction has been demonstrated by Waller (1987), Morth and Smith (1966) and Smith and Shumate (1970). It is therefore important to store specimens at the lowest practical temperatures. The common use of small scale portable dehumidifiers (either based on a heat pump or desiccant wheel) must be a cause for concern as both are responsible for elevated temperatures in store rooms.

The effects of changes in pH and oxygen concentration are difficult to determine in relation to museum collections as the existing work (Morth and Smith 1966, Smith and Shumate 1970) relates only to aqueous environments. However, a reduction in oxygen concentration in a storage environment should reduce the reaction rate. It is difficult to relate changes in pH to museum collections, however, it is probably not a significant factor.

There is clear evidence that bacteria can play a role in the oxidation of pyrite (Pugh, Hossner and Dixon 1984; Silverman 1967; Smith and Shumate 1970). However, the possible role of bacteria in the oxidation of pyrite associated with museum specimens has been reviewed and considered unlikely by Howie (1979b, 1992). This view is based on the fact that bactericides do not protect specimens and attempts to culture bacteria from oxidising museum specimens has been unsuccessful. Smith and Shumate (1970) stated that in a low pyrite to water ratio system the oxidation mechanism may be mainly bacteriological and in a high pyrite to water system the mechanism will be mainly chemical. Museum collections are analogous to a high pyrite to water system.

The possibility that trace elements play a role in pyrite oxidation (Caruccio 1972) has yet to be proved. The study described is limited with a small sample size. Caruccio (1972) does not prove a link between trace element distribution and pyrite stability. Other workers (Smith and Shumate 1970) dismissed the possibility. Therefore, it is probable that trace element distribution has no known significance for the stability of museum collections.

The damage caused to pyritic museum specimens by high RH has been recognised for many years. It was considered an important factor by Radley (1929) and Bannister (1933), although, both authors postulated

that other factors played a role. Bannister and Sweet (1943) concluded that "it has become only too obvious that a damp atmosphere speeds up the decomposition of pyrite". They recommended that specimens should never be treated with acid or washed in water.

Morth and Smith (1966) and Smith and Shumate (1970) showed experimentally that the rate of the oxidation reaction increased steadily with an increase in RH. Howie (1992) reviewed a paper by Wexler (1965) which stated that a mono-layer of water will form between 0% and 30%-60% RH and a multi-layer between 30%-60% and 90% RH on the surface of pyrite. Howie (1992) concluded that at between 30% and 60% RH sufficient water vapour is present to allow partially aqueous oxidation reactions to occur on the surface of the pyritic specimens. He stated that from this evidence the critical level of RH was possibly 30%. Waller (1987) calculated that the oxidation rate will double every 26% increase in RH. Experimental work by Howie (1979b) seemed to indicate that for many cases above a critical level of about 60% RH moisture absorption increased markedly in museum specimens and damage occurred. This related to work by Waller (1987, fig. 2) who showed the effect of RH on the hydration reactions that occur in the oxidation products. At about 60% RH a molar volume expansion of 256% occurs. This expansion is responsible for the cracking and damage associated with pyrite oxidation in museum specimens.

It is unclear to what extent the electrochemical mechanism of pyrite oxidation (Bang 1994) is influenced by RH in a museum environment. However, Howie (1979b) showed that specimens associated with carbon become unstable at a level of below 50% RH, about 10% lower than those without carbon. This may imply that for such specimens the electrochemical mechanism is playing a more significant role (Bang 1994). Therefore collections with a high carbon content need to be stored at levels of RH as low as possible, preferably less than 30%.

Work by Pugh, Hossner and Dixon (1984), Smith and Shumate (1970), Khawaja (1975) and others stated that the surface area of the pyrite will influence stability, while others (Lowson 1982) disputed the available evidence. However, this relationship is seen in museum collections (Howie 1979b, 1992). Specimens containing fine grained pyrite are more vulnerable than those with the massive form. The stability is again RH dependant and so levels in store rooms again need to be as low as possible.

Summary

From the above review it is apparent that RH is the critical environmental factor which controls the stability

of pyritic museum specimens. A level of not more than 30% has been recommended (Howie 1992) to provide protection. However, a practical study of the pyritic collections of the Hancock Museum, Newcastle upon Tyne has shown that after treatment with dry ammonia gas and storage in an environment with a RH of about 40% the collection has remained stable since 1985. (A more detailed account of the success of this conservation programme will be published separately). For most collections, without the use of micro-climates, 40% RH is a more realistic target for easily available dehumidification systems. Relative humidity of these levels will also prevent the damaging hydration reactions occurring in the oxidation products. Temperature also speeds up the rate of the oxidation reaction and so it is important not to allow store rooms to become too warm. Other factors may influence the rate of the oxidation reaction but may not have a direct effect on specimen survival. Once the main causes of instability of pyritic specimens in museum collections have been identified it is possible to determine the most effective conservation treatment.

Review of conservation treatments

Before a critique of the various conservation treatments is given it is important to consider the reasons for treating specimens. An effective rational for conservation treatments is given by Waller (1987), who refers to Radley (1929) and Gordon (1947). Both authors stated that the oxidation products are hygroscopic and enhance oxidation rates and Gordon (1947) stated that the removal or neutralisation of the acid decay products is essential to prevent the hydration reactions occurring and causing damage to specimens.

Howie (1977a, 1992) and Waller (1987) reviewed many of the conservation treatments which have appeared in the literature. Papers by Cornish and Doyle (1984), Bang (1994), and Booth and Sefton (1970) illustrated other techniques.

The literature described a number of methods which consist of four main approaches, firstly the neutralisation and or removal of the of the decay products, secondly placing a physical barrier between the specimen and atmospheric oxygen, either through coating the specimen or by placing it in an anoxic microenvironment. The third method involves disrupting the electrochemical process by reducing or removing the carbon content of specimens or providing some cathodic protection (Bang 1994). Treatment processes may consist of a combination of the above. The final method (Booth and Sefton 1970; Rixon 1976) presupposed the complicity of bacteria and concentrated on its inhibition.

The neutralisation of the products of the oxidation reaction has been an important part of the treatment process for many years. Bannister (1933) and Bannister and Sweet (1943) recorded that ammonia vapour was being used in the Mineral Department of the Natural History Museum, London. The same method was advocated by Rixon (1976). Firstly the products of decomposition were removed and then the specimen was exposed to vapour from 0.880 ammonia solution for several days. Secondly, the specimen was dried at 50°C and finally coated with Bedacryl 122X. Problems with this approach were highlighted by Howie (1977, 1979b) who stated that for large specimens, ammonia vapour only resulted in superficial neutralisation. He also stated that the air above ammonia solutions can have a RH of 70% and that even in these conditions oxidation reactions may occur. One solution to this problem is given by Birker and Kaylor (1986) and Waller (1987) who advocated the use of polyethylene glycol 400 as a humectant to reduce the RH in the ammonia vapour to a level which no longer causes concern. Another solution discussed by Howie (1977b, 1979a) was the use of dry ammonia gas, which provided effective results. Waller (1987) calculated that damage would occur, due to expansion during the reaction, when the specimen was acclimatised to an RH of less than 20%, which is virtually never the case. An account of the use of dry ammonia gas on pyritic material held by the Hancock Museum, Newcastle upon Tyne, will be published separately.

Rixon (1976) advocated the use of morpholine (1, 4,-tetrahydro oxazine), as a 5% solution in industrial methylated spirit to neutralise the decay products on specimens that were too large to be placed in a gas chamber. Howie (1977b) stated that such a process could be effective but it was difficult to use, because of its high toxicity (Clydesdale 1990) and its ability to dissolve consolidants and glues.

A further method to neutralise the products of the oxidation reaction is the use of ethanolamine thioglycollate (Cornish and Doyle 1984). The chemical was proposed because it will react with and remove acidic pyritic oxidation products as well as soluble and insoluble iron compounds. It is also soluble in ethanol or propan-2-ol as are the products of its reactions with pyrite oxidation products. The chemical can be an effective treatment in particular circumstances. An evaluation of this method will be published separately. The application of ethanolamine thioglycollate in the treatment of large specimens is described by Cornish, Doyle and Swannell (1995).

A different approach to the problem of the products of the oxidation reaction is to attempt to remove them rather than neutralise them. Such a procedure was proposed by Gordon (1947). He stated that some success had been achieved using concentrated hydrochloric acid. However, great care had to be taken to be sure that no other minerals were present which may be effected. The mechanical removal of the oxidation products from a specimen might also be an option, however this is normally only attempted together with neutralisation.

The coating of specimens with waxes or soluble plastics is a traditional method of attempting to preserve specimens and has been used by itself or as part of a treatment process (Bather 1908; Radley 1929; Rixon 1976). Howie (1979b) experimentally tested the effectiveness of a number of plastic films. A number of pyritic museum specimens were coated with Butvar B98, Bedacryl, Vinylite and compared with a control sample. The results of this work showed that such films were ineffective in preventing deterioration. The reason for this was that all such films are permeable to water vapour to a greater or lesser extent (Thompson 1978), they are easily damaged by abrasion, and once oxidation starts are broken down by the decay products. Radley (1929) also expressed reservations about the effectiveness of such films. A different form of the barrier method is the storage of vulnerable specimens in inert liquids such as mineral oils, liquid paraffin, glycerol, carbon tetrachloride (Bather 1908) or silicone fluids (Rixon 1976). Richardson (1842) and Bather (1908) described the practice of keeping specimens under water. However, the latter author recorded that such a storage medium does not prevent the disintegration of specimens. Rixon (1976) described how, because the removal of mineral oils and liquid paraffin from specimens was difficult, they were often transferred to glycerol. However, this medium is hygroscopic and difficult to maintain successfully in the long term. It proved a problem to remove when specimens were transferred to silicone fluids in the early 1960s. Such a programme was carried out in the Natural History Museum in London and the specimens are now mainly stable 37 years later, with very few showing signs of problems (Tiffany Foster, pers. comm. 1997).

The use of anoxic microenvironments described by Burke (1996) is a possible new way of preserving specimens. He detailed the materials that are needed to form a barrier film and commercially available oxygen absorbers. It is clear that such an approach needs a long-term and detailed evaluation to determine its effectiveness. The existing literature only deals with the effect of varying oxygen concentration on pyrite oxidation in the aqueous phase (Morth and Smith 1966, Smith and Shumate 1970). However, it is likely that that a similar dependence will occur in air. Potential problems with the suggested oxygen absorber, 'Ageless',

produced by the Mitsubishi Gas Chemical Company, are that its effectiveness reduces at low relative humidities and that it generates heat when removing oxygen from an environment. Particular types of 'Ageless' may cause increased relative humidities, and determining oxygen concentration in the micro-climate over the longer term may be difficult. Also, the removal of oxygen from a sealed microclimate will result in a 20% volume reduction, which may cause problems. The greatest difficulty is that which is common to all micro-climates, in that the specimens are safe as long as they are not being used. As soon as a specimen is removed for research or some other purpose it will become increasingly unstable in its new environment. The above methodology requires therefore more evaluation as to whether it is applicable to the storage of pyritic specimens in museums.

Bang (1994) proposed the use of a plasma-ashing (Hollahan and Bell, 1974) as a conservation treatment. The rationale behind such an approach is that by the removal of carbon, the electrochemical process responsible for the decomposition of specimens is disrupted. The paper described a number of experiments on fossil material and the apparent success that had been achieved with part of a whale vertebral centrum, however other specimens did not provide conclusive results. The problem with such an approach is that it tends to make specimens brittle and so some sort of artificial strengthening is required. It is also difficult to treat large specimens. Bang (1994) also discussed the possibility of preserving specimens by placing them in a dense mist of electrons providing cathodic protection. The above is interesting as it may provide a new approach to the conservation of pyritic museum specimens. However, the method is still new and it requires extensive evaluation.

As has been stated earlier the complicity of bacteria in the oxidation of pyrite in dry environments, (and so museum specimens), is considered unlikely (Howie 1979, Smith and Shumate 1970). However, as part of this review it is worth mentioning treatments that were used when such a view was considered correct. Booth and Sefton (1970) described the use of 4-chloromeresol as a way of inhibiting the growth of Thiobacilli and Ferrobacilli and so preserving pyritic museum specimens. Rixon (1976) described the use of Cetrimede and Savlon as anti-bacterial agents.

Conclusion

From the above review it is possible to conclude that for museum specimens oxidation has a chemical/ electrochemical pathway. The main cause of damage to specimens are the hydration reactions that occur in the products of the oxidation reaction. The oxidation rate as well as the hydration reactions are directly related to levels of RH. The electrochemical processes are enhanced by the presence of carbon which forms a galvanic corrosive system. Stability of specimens will probably be achieved by storage in a RH of less than 30% although in practice levels up to 40% may also give protection.

The treatment currently recommended is neutralisation and removal of the products of the oxidation reaction, using ammonia vapour, with PEG 400 as a humectant, dry ammonia gas or ethanolomine thioglycollate. Specimens, once treated, must be stored in a low RH environment. The use of plasma-ashing or anoxic environments provide an interesting line of research but are as yet unproven.

The literature lacks any long term evaluation of treatment methods and studies need to be carried out to determine the effectiveness of what is currently seen as best practice. An account of the successful conservation programme carried out on the pyritic collections of the Hancock Museum, Newcastle upon Tyne will be published separately. The methods used, dry ammonia gas and storage in an RH of 40-43%, has stabilised the collection since 1984. However, whether the treatment process, the storage conditions or a combination of both are responsible for specimen stability is unclear. An unpublished review of treated specimens in the Natural History Museum, London (Adrian Doyle pers. comm. 1997), concluded that treatment methods (ethanolamine thioglycollate, ammonia vapour with PEG400) were effective. However, without detailed records of the condition of specimens before treatment definite conclusions were difficult to achieve. Studies are at present being carried out at the Canadian Museum of Nature (Robert Waller pers. comm. 1996) which consider oxidation as a function of RH and chemical treatment. Preliminary results imply that none of the chemical treatments reduce oxidation rates by more than ten fold. The suspicion is that the stability of specimens relates more to preventing the RH dependant hydration reactions occurring in the products of the oxidation reaction rather than the oxidation reaction itself. The implication is that whilst treatment will help to reduce the oxidation reaction, the main way to stabilise specimens is to keep them in a level of RH which will prevent the hydration reactions occurring.

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References

- BANG, B.S. 1994. Framboidal pyrite and associated organic matrices, a risky composite for preservation of fossils. *In* Kejser, U. B. (ed.), *Surface treatment: Cleaning, Stabilization and Coatings* Pre-print, Copenhagen September 1994 IIC Nordic Group, Danish Section, XIII Congress, Copenhagen. 7-11.
- BANNISTER, F.A. 1933. The preservation of pyrite and marcasite. *Museums Journal* **33**, 72-75.
- BANNISTER, F.A. and SWEET, J.M. 1943. The decomposition of pyrite. *Museums Journal* **43**, 8.
- BATHER, F.A. 1908. The preparation and preservation of fossils. *Museums Journal* **8**, 76-90
- BIRKER, I. and KAYLOR, J. 1986. Pyrite disease: case studies from the Redpath Museum. *In* Waddington, J. and Rudkin, D. M. (eds.), Proceedings of the 1985 workshop on the care and maintenance of natural history collections. *Life Science Miscellaneous Publications*, Royal Ontario Museum, 21-27.
- BOOTH G. H. and SEFTON, G. V. 1970. Vapour phase inhibition of thiobacilli and ferrobacilli: a potential preservative for pyritic museum specimens. *Nature* **226**, 185-186.
- BURKE, J. 1996. Anoxic microenvironments: a simple guide. *SPNHC Leaflets*, 1, 1.
- CARUCCIO, F.T. 1972. Trace element distribution in reactive and inert pyrite. *Proceedings of the 4th symposium on coal mine drainage*, Pittsburgh, 48-54.
- CLYDESDALE, A. 1990. *Chemicals in conservation, a guide to possible hazards and safe use.* Conservation Bureau, Scottish Development Agency, Edinburgh.
- CORNISH, L. and DOYLE, A. 1984. Use of ethanolamine thioglycollate in the conservation of pyritised fossils. *Palaeontology* **27**, Part 2, 421-424.
- CORNISH, L, DOYLE, A.M. and SWANNELL, J. 1995. The gallery 30 project: conservation of a collection of marine reptiles. *Conservator* **19**, 20-24.
- GORDON, S.G. 1947. Preservation of specimens of marcasite and pyrite. *American Mineralogist* **32**, 589.
- HOLLAHAN, J.R. and BELL, A.T. 1974. *Techniques and applications of plasma chemistry*. John Wiley and Sons, London, 403 pp.
- HOWIE, F.P.M. 1977a. Pyrite and conservation Part 1: historical aspects. *Newsletter of the Geological Curators' Group* 1, 457-465.
- HOWIE, F.P.M. 1977b. Pyrite and conservation, Part 2. Newsletter of the Geological Curators' Group 1, 497-512.

- HOWIE, F.M.P. 1978. Storage environment and the conservation of geological material. *Conservator* **2**, 13-19.
- HOWIE, F.M.P. 1979a. Physical conservation of fossils in existing collections. *Newsletter of the Geological Curators' Group* **2**, 269-280.
- HOWIE, F.M.P. 1979b. Museum climatology and the conservation of palaeontological collections. *In* Bassett, M. G. (ed.), Curation of palaeontological collections. *Special Papers in Palaeontology* 22, 103-125
- HOWIE, F.M.P. 1986a. Conserving natural history collections: some present problems and strategies for the future. *In* Waddington, J. and Rudkin, D.M. (eds), Proceedings of the 1985 workshop on care and maintenance of natural history collections. *Life Science Miscellaneous Publications*. Royal Ontario Museum, Canada 1.
- HOWIE, F.M.P. 1986b. An electrochemical mechanism for the oxidation of pyrite in museum-stored specimens. *In* Waddington, J., and Rudkin, D.M. (eds), Proceedings of the 1985 workshop on care and maintenance of natural history collections. *Life Science Miscellaneous Publications*, Royal Ontario Museum, Canada 28.
- HOWIE, F.M.P. 1992. Pyrite and marcasite. *In* Howie, F. M. P. (ed.), *The care and conservation of geological material, minerals, rocks, meteorites and lunar finds.* Butterworth-Heinemann, Oxford, 70-84.
- KIM, H.W. 1964. *Vapour phase oxidation of pyrite*. Unpublished M.Sc. Thesis. The Ohio State University.
- KHAWAJA, I.U. 1975. Pyrite in the Springfield coal member (V), Petersburg Formation, Sullivan County, Indiana. *Special Report No. 9. Geological Survey Indiana* 1-19.
- LORENZ, W.C. and TARPLEY, E.C. 1963. Oxidation of coal mine pyrites. *United States Bureau of Mines*, *Report* **6247**, Pittsburgh, Pa.
- LOVE, L.G. 1958. Microorganisms and the presence of syngenetic pyrite. *Quarterly Journal of the Geological Society of London* 113, (for 1957), 429-440.
- LOWSON, R.T. 1982. Aqueous oxidation of pyrite by molecular oxygen. *Chemical Reviews* **82**(5), 461-497.
- LUTHER, G.W. III. 1987. Pyrite oxidation and reduction: molecular orbital theory considerations. *Geochimica et Cosmochimica Acta* **51**, 3193-3100.
- MORTH, A.H. and SMITH, E.E. 1966. Kinetics of thesulphide to sulphate reaction. *American Chemical Society, Division of Fuel Chemistry, Pre-prints* **10**(1), 83-92.
- NORDSTROM, D.K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. *In* Kittrick, J.A., Fanning, D.S. and Hossner, L.R. (eds), Acid sulfate weathering. *Soil Science Society of*

- America, Special Publication 10, 37-56.
- ODDY, W.A. 1977. The conservation of pyritic stone antiquities. *Studies in Conservation* **22**, 68-72
- PETERS, E. 1984. Electrochemical mechanisms for decomposing sulphide minerals. *Proceeding of the Electrochemical Society* **84**, 343-361.
- PUGH, C.E., HOSSNER, L.R. and DIXON, J.B. 1984. Oxidation rate of iron sulphides as affected by surface area, morphology, oxygen concentration, and autotrophic bacteria. *Soil Science* **137**(5), 309-314.
- RADLEY, E.G. 1929. The preservation of pyrite and other fossils. *The Naturalist*, April 143-146, May 167-173, June 196-202.
- RICHARDSON, G.F. 1842. *Geology for beginners*. Schulze and Co. London, xvii+366 p.
- RIXON, A. E. 1976. Fossil animal remains: their preparation and conservation. The Athlone Press, University of London. London, vi+304 p.
- RUST, G.W. 1935. Colloidal primary copper ores at Cornwall Mines, Southeastern Missouri. *Journal of Geology* **43**, 398-426.
- SCHOPF, J.M., EHLERS, E.G., STILES, D.V. and BIRLE, J.D. 1965. Fossil iron bacteria preserved in pyrite. *Proceedings of the American Philosophical Society* **109**(5). 288-305.
- THOMSON, G. 1978. *The museum environment.* Butterworths, London, 293 p.

- SILVERMAN, M. P. 1967. Mechanism of bacterial pyrite oxidation, *Journal of Bacteriology* **94**, 1046-1051.
- SMITH, E.E. and SHUMATE, K.S. 1970. The sulphate to sulphide reaction mechanism. *Water Pollution Control, Research Series, Ohio State University Research Foundation*, Columbus, Ohio, 129 pp.
- TEMPLE, K.L. and KOEHLER, W.A. 1954. Drainage from bituminous coal mines. West Virginia University Engineering Experimental Station Bulletin 25.
- WALLER, R. 1987. An experimental ammonia gas treatment method for oxidised pyritic mineral specimens. *Triennial Report, ICOM Committee for Conservation*, 623-630.
- WALLER, R. 1989. Pyrite oxidation studies. *Canadian Conservation Institute Newsletter*, Spring/Summer10.
- WEXLER, A. 1965. *Moisture and Humidity*. Volume 3. Reinhold, New York.
- WILKIN, R.T. and BARNES, H.L. 1997. Formational processes of framboidal pyrite. *Geochimica et Cosmochimica Acta* **61**, 323-339.
- WILSON, A.H. and ZUBERER, D.Z. 1976. Some microbiological factors associated with surface-mine reclamation. West Virginia University Experimental Station Bulletin 645T.

