GEOLOGICAL CURATOR

GCG

Volume 11 Number 1

PYRITE OXIDATION: WHERE ARE WE NOW?

THE GEOLOGICAL CURATOR

VOLUME 11, NO. 1

GEOLOGICAL CURATORS' GROUP

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The Group is affiliated to the Geological Society of London. It was founded in 1974 to improve the status of geology in museums and similar institutions, and to improve the standard of geological curation in general by:

- holding meetings to promote the exchange of information
- providing information and advice on all matters relating to geology in museums
- the surveillance of collections of geological specimens and information with a view to ensuring their wellbeing
- the maintenance of a code of practice for the curation and deployment of collections
- the advancement of the documentation and conservation of geological sites
- initiating and conducting surveys relating to the aims of the Group.

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Cover: see Figure 4 in Larkin inside.

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This issue is dedicated to Joy Irving, a former Collections Assistant in the Oxford University Museum of Natural History, whose work on pyrite oxidation has been an inspiration to many colleagues in the field.

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Other Papers

EDITORIAL

This packed issue, the first of Volume 11, is a state-of-the-art summary of a topic that concerns virtually every geological curator at some time - that of pyrite oxidation. The thematic set of papers herein were inspired by the efforts of Lu Allington Jones who organised a well-attended joint meeting between the Natural History Museum and the Geological Curators' Group. This took place on the 10th May 2018, and provided valuable practical training for participants as well as theoretical overview and detail. Whilst it has taken over a year to get some of the oral and poster presentations from that meeting into print here, the timetable has permitted a number of extra papers on the topic, which enrich the value of this collection. My special thanks go to Lu Allington-Jones for her efforts in ensuring the thematic set was ultimately delivered.

This issue is dedicated to Joy Irving, a former Collections Assistant in the Oxford University Museum of Natural History, whose work on pyrite oxidation has been an inspiration to many colleagues in the field. Joy died on the 13 April 2019 and despite her serious illness, she completed her paper with Phil Hadland for this volume a week before she died. An obituary completes this issue on page 109.

Of course, other submissions appear and with a plethora of thematic sets in the journal (recently and in forthcoming issues), they can not be held over without very good reason, so this issue has other papers of potential interest to many readers. I especially want to thank all of the referees for papers in this issue, many of whom have gone above and beyond expectations in completing their reviews. This valuable effort results in significantly better papers and is much appreciated by the editor, but also I am sure, by readers.

Matthew Parkes

THE ROLE OF PYRITE IN FOSSILISATION AND ITS POTENTIAL FOR INSTABILITY

by Kieran Miles

Miles, K. 2019. The role of pyrite in fossilisation and its potential instability. *The Geological Curator* 11 (1): 3-8.

Pyrite often forms in organic-rich marine sediments through bacterial action. Bacteria reduce organics to form bisulphide, which reacts in turn with dissolved iron in seawater to form pyrite. Consequently, it is frequently found in stratigraphic formations that consist of marine clays. Pyrite can be involved in fossilisation through a number of ways, including complete replacement, as infill in permineralised bone, or simply as microcrystals finely disseminated through the fossil and matrix. Replacement by pyrite can often be easily recognised: the fossil may have a gold or brassy metallic lustre. Infill is harder to recognise, and disseminated pyrite even more so. Pyrite in fossils may be stable or unstable- in its stable form, pyritised fossils will generally retain their shiny, metallic appearance. Pyrite preservation and stability can vary even within the same specimen. Fossils preserved in pyrite can be prone to oxidation, particularly at high relative humidities. There are a number of signs that indicate oxidation is occurring, depending on the severity of the condition. One or more of the following may be present: a sulphurous smell, white or yellow powdery crystals on the surface of the specimen, expansion cracks, as well as acid burns on associated labels, boxes and drawers. Such burns often have a characteristic ovoid appearance. If left unchecked, pyrite oxidation can completely destroy a specimen and its labels.

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Introduction to pyrite

The mineral pyrite, commonly known as 'fool's gold' or sometimes iron pyrites, is a form of iron disulphide (FeS_2). It has a shiny, metallic lustre, and is often a brassy, golden or silver colour. It is very common worldwide- the most common sulphide mineral on the Earth' surface (Rickard 2015). It can exhibit a wide variety of crystal habits (Figure 1 for example), with crystals varying from microscopic grains all the way up to large, impressive cubes, such as the famous examples from Navajun in Northern Spain, where a single crystal can grow to up to 19cm across (Rickard 2015).

The range of crystal structures that pyrite can show include cubic (the most common, usually with striated faces), pyritohedral (the second most common, an unusual structure of twelve faces, each with five sides, i.e. a pentagonal dodecahedron), octahedral (essentially two pyramids, base-to-base) and, rarely, diploid (a complex structure of twenty-four faces each with four sides) (Canfield and Raiswell 1991).

Pyrite can also exhibit several different 'textures' - the characteristics and contact relationships of the crystals (Canfield and Raiswell 1991) - particularly framboids and clusters. Framboids are small, globular aggregates of pyrite crystals, and are superabundant; estimates suggest that there are 10 billion times more pyrite framboids in the world than sand grains (Rickard 2015). The name derives from their raspberry-like appearance. Usually too small to see without a hand lens, they are generally made up of spheres of tiny cubic crystals, each less than 5µm in diameter. Clusters are less ordered and more crudely spherical, with crystals often larger than those comprising framboids.

Pyrite formation

Pyrite forms by bacterial action in marine sediments, especially clays. Anaerobic bacteria first reduce seawater sulphate to sulphide, which then reacts with iron to form pyrite, either directly or via a monosulphide precursor.

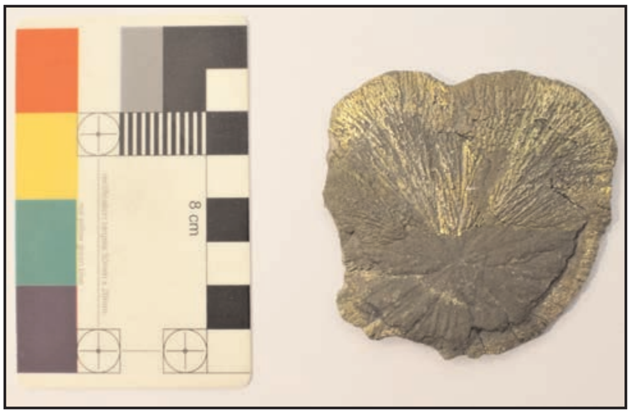

Figure 1. A 'pyrite sun' or 'pyrite dollar', from Illinois in the USA, where the pyrite concretions grew under such pressure from the surrounding slate that they were forced to grow in a compressed, radiating manner. Unregistered specimen, NHM handling collection.

There are four prerequisites for the formation of pyrite: anoxic conditions, organic matter, a sulphate supply and iron (Fisher and Hudson 1987).

1. Anoxic conditions.

Sulphate-reducing bacteria need this to function. This does not necessarily mean the whole environment needs to be anoxic - there might be an anoxic layer of sediment beneath oxygenated sediment in oxygenated waters. This can also be easily created by bacterial decay, as a large concentration of decaying organic matter can create a natural anoxic microenvironment around the remains. Anoxic conditions can also be found in void spaces, such as burrows or ammonite shell chambers.

2. Organic matter.

This is necessary as it is the material on which sulphate-reducing bacteria feed. In addition, as previously mentioned, the presence of decaying organic matter can actually supply the anoxic conditions required.

3. Sulphate supply.

The main source of sulphate in marine sediments is from seawater, which is often rich in sulphates derived from the oxidation of sulphite ores.

4. Iron.

This is necessary for the conversion of hydrogen sulphide to iron sulphide. Iron is supplied to the sediment in detrital minerals, as iron oxide coatings on grains, or it can be dissolved in the water column.
So the supply of organic matter, the amount of available iron, and the sulphate content of the water can all be limiting factors in how much pyrite can form in an environment. Pyrite can form in freshwater environments, but it is far less common - the major constraint here is the sulphate supply, as there is usually very little in freshwater.

Pyrite and fossilization

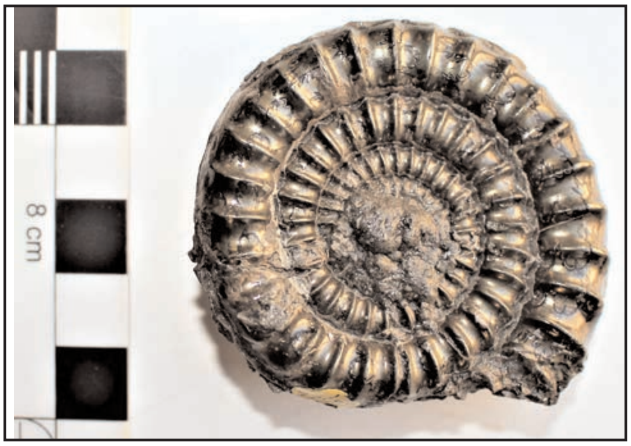

*Figure 2. Pyritised ammonite (*Echioceras elegans*) from Charmouth, Dorset, with suture lines visible. (NHMUK PI C 26766)*

There are a number of ways that pyrite can be involved in the fossilisation process. These can include:
Permineralisation. Pyrite may be precipitated in cellular cavities and pore spaces, for example in fossil bone.

Replacement (also called 'pyritisation'). In the aragonitic shells of ammonites for example, calcium carbonate can be gradually replaced by pyrite. This is likely to occur in areas where the seawater is undersaturated with carbonates, but over-saturated with sulphates. In the right conditions, this can occur surprisingly quickly - there are even recorded cases of pyritisation beginning in bivalve shells while the animal is still alive (Clark and Lutz 1980).

Mineral casts and moulds. Pyrite can fill in the void spaces around or inside an organism; if the original shell is dissolved, a perfect internal cast can be left behind. Again, there are good examples of this in ammonites, where impressions of the suture lines can often be visible (Figure 2).

Coatings and linings. These can build up on the outside or inside of a fossil, respectively - again ammonites are a good example, as pyrite stalactites have been found growing inside the chambers on some specimens (Hudson 1982). Thick coatings of pyrite are sometimes referred to as 'over-pyrite', and when it encrusts a fossil it can obscure morphological details. This can occur if the seawater is already oversaturated with carbonates as well as sulphates, leading to pyrite being precipitated directly on to the shell (Canfield and Raiswell 1991).

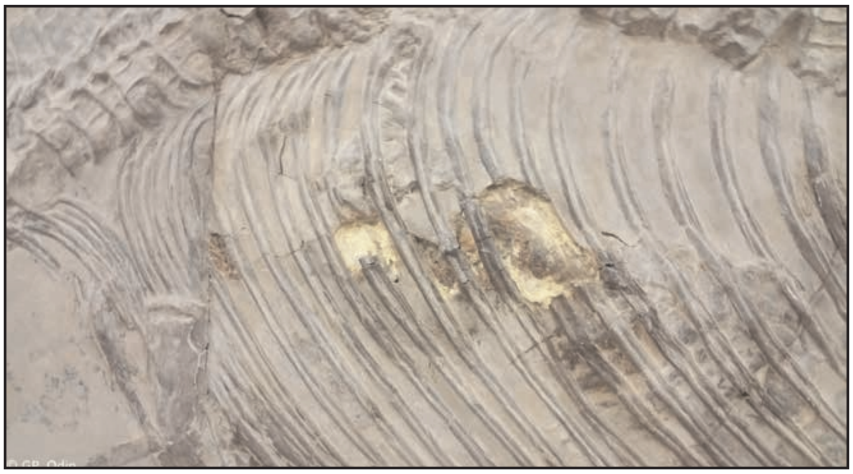

Figure 3. Pyrite oxidation in a concentrated mass in the ribcage area of an ichthyosaur. Specimen from the palaeontological collections of Sorbonne Universite, Paris.

Another interesting example of pyrite coatings is in the presence of biofilms (Borkow and Babcock 2003). Bacterial coatings on the surface of decaying organic matter can themselves be coated with pyrite, as can microbial assemblages around the edges of the decaying matter. The former tends to result in a thin pyrite crust, while the latter results in the growth of a pyrite halo; these halos appear to be the precursor to the formation of pyrite concretions.

Pyrite may also be found as microscopic crystals disseminated finely through a fossil and/or matrix, especially as framboids in sediment. Different modes of pyrite preservation can occur before, during and after diagenesis - and as pyrite formation is so tied to environmental conditions, a single fossil may show combinations of these different types of fossilisation. An interesting example of this is the often observed occurrence of pyritic gastric masses in the thoracic regions of ichthyosaur fossils; possibly the stomachs of these animals were thick and durable, and acted as a nucleus for pyrite deposition. There seems to be a tendency for these gastric masses to be badly affected by oxidation - good examples of this can be seen in ichthyosaur and marine crocodile specimens collected from the Posidonia shale from Holzmaden, Germany (Figure 3).

Preservation by pyrite can be beneficial - infill in pore spaces helps bones resist compaction, for instance in the Oxford Clay, leading to wonderful three-dimensionally preserved vertebrate specimens; and replacement can sometimes lead to exceptional soft-tissue preservation.

Soft-tissue pyritisation is rare, and is believed to require quite specific physical and chemical conditions, including rapid burial, stagnation, and sometimes cyanobacterial coatings (Canfield and Raiswell 1991). One way this can happen is by pyritisation of a layer of bacteria on the soft tissues, which leaves a perfect outline of the original material. One famous example of this is the trilobites at Beecher's Trilobite Bed in New York State, where the antennae, legs and even gills of the trilobites are preserved in this manner.

The other site that is known for this style of preservation is the Hunsruck Slate in West Germany, which shows a diverse assemblage of Devonian marine life, including fantastically well-preserved arthropods, echinoderms and even entirely soft-bodied animals such as annelid worms.

Pyrite oxidation

Pyrite can be unstable, and react with atmospheric oxygen and water. This oxidation reaction is often referred to as 'pyrite decay', (or sometimes 'pyrite rot' or 'pyrite disease') and can pose a serious risk to fossil collections. Oxidation can be bacterial, molecular or electrochemical. In museum environments, the reaction will usually follow one of the latter two pathways (Newman 1998).

The simplified version of the reaction is as follows:
$\mathbf{4FeS_2 + 13O_2 + 2H_2O > 4FeSO_4 + 2H_2SO4 + 2SO_2}$

The by-products of this reaction usually comprise sulphur dioxide, sulphuric acid and hydrated ferrous sulphates, but can vary depending on the composition of the fossil or matrix- for example, gypsum can sometimes form as a secondary mineral (Odin *et al* 2018).

Factors increasing the rate of the reaction include high temperature, high humidity, and fine grain size of pyrite. Microcrystalline and framboidal forms seem to be most reactive, as they have a very high surface area to volume ratio. In contrast, compact, well-crystallised forms generally seem to be very stable.

A major factor is high humidity - the reaction greatly accelerates above 60% RH. Once the reaction has started, mineral hydrates can continue to form as low as 30% RH. Exposure to inappropriate humidity can, in some cases, be enough to trigger a reaction in a matter of days (Newman 1998).

The decay products are extremely sensitive to changes in hydration and these hydration reactions are a major cause of damage to specimens. Because iron sulphates adsorb water from the atmosphere to become hydrated, the reaction can become self-sustaining.

Commonly affected formations

It has long been noticed by fossil collectors, researchers and curators that fossils from certain stratigraphic horizons seem to be more at risk from pyrite oxidation than others. In the UK for example, the Oxford Clay of Peterborough, The Lias of Lyme Regis, the Gault Clay from Folkestone and the London Clay at the Isle of Sheppey are all known to be problematic. Other formations commonly affected by the problem include the Speeton Clay, the Barton Clay, as well as various Carboniferous coal-bearing formations which can also be associated with unstable pyrite. A list of sites in the UK that yield fossils with a tendency to suffer from pyrite oxidation can be found elsewhere in this volume (see Larkin *et al* 2019).

Most of these formations have a high amount of microcrystalline and/or framboidal pyrite, forms which have a higher potential to react. In addition, some of these, such as the London Clay, also contain a high amount of organic carbon - this can increase the permeability of the sediment or fossil, providing channels that can allow the ingress of oxygen or water. It is possible that carbon may also play a role in the electrochemical oxidation reaction (Howie 1979).

It also seems that the chemistry of the clay minerals present can have an effect. For example, a team in Denmark (Holmberg 2000) noticed that of two fossil whale specimens collected from the same formation of Miocene clay, one was badly affected by oxidation while the other seemed to be stable. They also noted that the clay matrix of the affected specimen was dark grey, while the other was light grey and, after analysing it, found a high concentration of the clay mineral smectite in the darker clay. Their conclusion was that fossils preserved in smectite-rich clays would be more susceptible to oxidation, as smectite has a high absorption capability as well as a low pH.

Signs of Decay

A loss of surface shine and the distinctive sulphurous smell are often early warning signs that oxidation is occurring. As the reaction continues, any or all of the following may also be evident: a powdery efflorescence on the surface of the specimen; expansion cracks in the fossil; and acid burns on boxes, labels etc.

Powder. This powdery efflorescence can be white, grey, yellow or sometimes greenish, and often has a cigarette-ash like appearance (Figure 4). It is usually composed of various ferrous sulphates, and can be a health hazard.

Expansion cracks. These occur as hydrated ferrous sulphates form - as they are several times the volume of the original mineral, they force the specimen apart from within, causing it to crack and crumble. Most damagingly, above 60% RH, the 1 to 7 hydrate transition occurs, resulting in a 256% volume expansion. This hydrate, melanterite, is the main cause of specimens cracking and falling apart (Irving 2001).

Acid burns. These happen as the sulphuric acid attacks lignin in paper, card and wood - this can cause serious damage to associated labels, boxes, even drawers and shelves. The acid is highly corrosive and in extreme cases can burn a hole right through a drawer. It often leaves a characteristic ovoid burn.

Sulphuric acid also acts as a solvent, removing passive oxide coatings and tarnishes and so exposing more fresh surface to react; in addition to this, it also acts as an electrolyte, further supporting any electrochemical oxidation that may occur (Irving 2001).

The decay products can actually react with other minerals in some cases, causing further problems - calcium carbonate fossils can suffer if the sulphate by-products react with them, causing gypsum to be formed - which, as a hydrated form of calcium sulphate, can also cause expansion cracking. Because of the corrosive nature of some of the oxidation products, care should be taken when handling or working with affected specimens. Powdery efflorescence should be carefully brushed away under extraction, and gloves should be worn to protect against sulphuric acid.

The Natural History Museum in London holds a very large (estimated 8 million) fossil collection, many thousands of which are threatened by pyrite oxidation. The Airless project was set up in 2015 to identify and treat at-risk fossil and mineral specimens. The project has been running for more than three years now; to date, nearly 8,000 specimens have been processed. For details of some of the past and present methods of combating pyrite decay at the

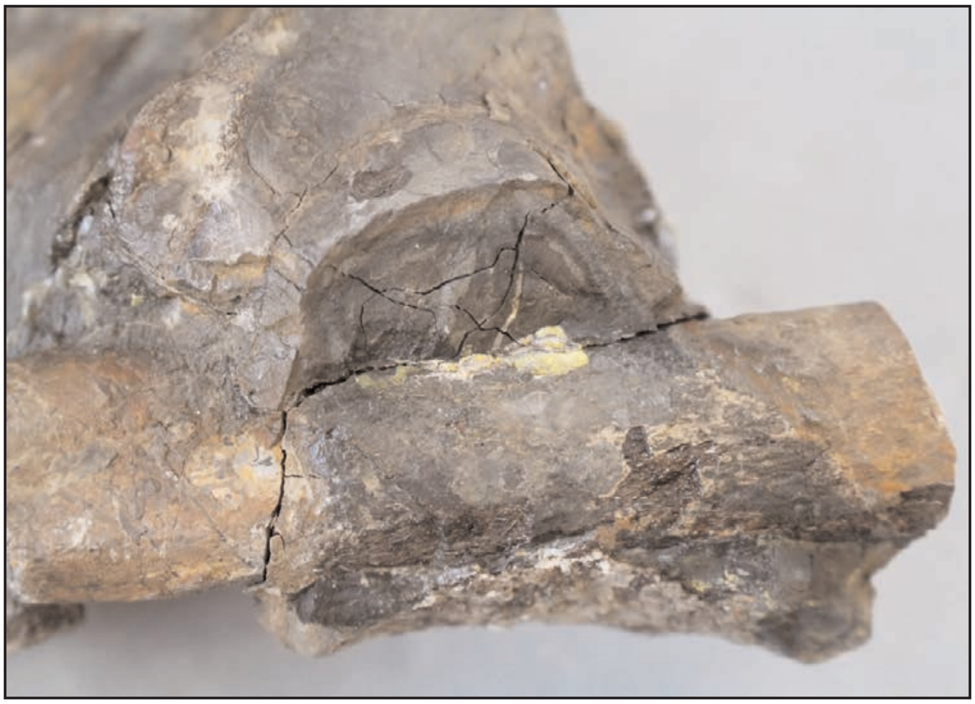

Figure 4. Expansion cracks and powdery efflorescence on a plesiosaur bone from Kimmeridge, Dorset (NHMUK PV R 5739).

NHM, see Fenlon and Petrera (2019) elsewhere in this volume.

Conclusion

Pyrite is a commonly found mineral that forms readily in the right environments, constrained only by a supply of organic material, sulphates and dissolved iron. Although large, well-formed crystals are very recognisable, its presence can sometimes be much harder to detect, particularly the abundant microcrystals. Pyrite can become involved in the fossilisation process in a number of ways, and this can cause problems for collectors and curators of fossils. Although it can be perfectly stable, attractive and lead to exceptional preservation, some forms, especially very fine-grained examples, can be prone to a highly destructive oxidation reaction.

Because of the unstable nature of some of this material, care should be taken in how these fossils are stored, as environmental conditions - such as high humidity - can have a catastrophic effect. If nothing is done to prevent it, pyrite oxidation can cause irreversible damage to, or even the complete destruction of, scientifically important specimens. It is vital that anyone involved in the care of collections containing susceptible material is aware of the signs of pyrite oxidation (a sulphurous smell, powdery efflorescence, expansion cracking and acid burns) so that the reaction can be slowed or halted as quickly as possible.

Although pyrite oxidation has been long recognised and well-studied, as a major threat to fossil and mineral collections it is always worth highlighting the issue. While many of the details are now well understood, there are still aspects of the subject that remain mysterious. The tendency for pyrite oxidation to occur in concentrated masses within the thoracic regions of marine reptiles from various localities in particular warrants further investigation in the future.

Acknowledgements

Grateful thanks to Lu Allington-Jones (The Natural History Museum, London) for help finding references, and for organising the 'Pyrite Oxidation: Where are we now?' seminar and workshop day at the NHM, and to the other organisers and attendees of this event, as well as Anna Fenlon and Lucia Petrera, conservation technicians on Project Airless at the museum.

Thanks are also due to Giliane Odin (University College Cork) and Sorbonne Universite, Paris, for the use of the image of the ichthyosaur specimen showing a pyritic mass in its thoracic region, and to the reviewers and editor of this journal.

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PYRITE OXIDATION: A HISTORY OF TREATMENTS AT THE NATURAL HISTORY MUSEUM, LONDON

by Anna Fenlon and Lucia Petrera

Fenlon, A. and Petrera, L. 2019. Pyrite oxidation: a history of treatments at the Natural History Museum, London. *The Geological Curator* 11 (1): 9-18.

Whilst surveying the palaeontology collections at the Natural History Museum London (NHM), a team of Conservation Technicians working on 'Project Airless' (a re-storage project for actively deteriorating pyritic specimens) kept a record of specimen labels describing past methods for treating pyrite oxidation, ranging from 'boiling in common soda' to treating with 'Savlon'. This prompted further research into the thinking behind these approaches, and resulted in a historical review of treatments used at the NHM and how they compare to current methods.

The oxidisation of unstable pyritic material became a prominent issue during the development of geological collections in the 19th Century, when early collectors provided most insight into best practice storage of affected specimens, although it was not until the 20th century when more intensive research was conducted and recommended treatments for deteriorating pyritic material began to circulate. Regardless of the treatment, however, once specimens were returned to storage conditions of high relative humidity (RH) the reaction would often recur; this instigated the need for a more preventative approach focussing on reducing, if not eliminating, the key agents involved in the oxidation process: oxygen and high RH.

Project Airless is the latest attempt at the NHM to combat pyrite oxidation on a large scale by storing affected specimens in anoxic microenvironments to prevent further deterioration. Severely affected specimens are also exposed to ammonia vapour in a method which has evolved from earlier treatments.

Although commonly referred to as The Natural History Museum London, the museum was officially known as The British Museum (Natural History) until 1992, so for the purposes of this article the 'BM(NH)' will be referred to until this date, and the 'NHM' thereafter.

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Introduction

Pyrite (FeS_2) is an iron sulphide mineral commonly associated with fossilised material and known as 'fool's gold' because of its superficial similarity to the valuable metal. It develops most commonly in cubic crystal formations, and can be unstable, oxidising in conditions of high humidity and oxygen.

The oxidation reaction that occurs in these conditions is as follows:

$$\mathbf{4FeS_2 + 13O_2 + 2H_2O \text{ -> } 4FeSO_4 + 2H_2SO4 + 2SO_2}$$

The process has been described as pyrite 'rot', 'disease' and 'decay', with common symptoms including cracking, acid damage to specimens and surrounding media, and a sulphurous smell.

One of the earliest empirical observations of the effects of pyrite oxidation was made in the 17th century by John Mayow, who described how the interaction of oxygen and the "sulphur portion of ore" could form acidic by-products (Howie 1992). It was the neutralisation of these by-products that has long been regarded as a priority for most remedial treatments in order to prevent further damage, and the concept still forms the basis of modern treatments such as exposure to ammonia vapour and the application of ethanolamine thioglycollate (ET).

Measures taken to prevent the reaction from occurring have involved coating specimens with a range of varnishes and waxes, storing in various liquids, reducing the relative humidity of storage environments and present day anoxic storage using barrier film. All of these methods are attempts to provide a "physical barrier" (Newman 1998) to protect the specimen from oxygen and moisture, two of the active agents recognised in pyrite decay (Howie 1977 a).

Evolution of neutralisation treatments

During the 17th and 18th centuries, interest in the nature of fossils grew alongside the number of collectors, one of whom was Edward Jacob (1713-1788), who stated in his personal collection catalogue that a "pyritical matter" was going to destroy his specimens from the Isle of Sheppey: "the salts thereof shoot and destroy them" (Jacob in Torrens (cover), 1977). Like Jacob, many other collectors were also looking for a remedy to prevent this deterioration, and thus the need for sharing knowledge and information started to develop (Torrens 1977).

Some of the earliest instructions for the amateur treatment of pyrite oxidation were put forward by George Fleming Richardson, Assistant in the Mineralogy and Geology Branch at the BM(NH). In his book *Geology for beginners* (1842), Richardson suggests boiling specimens then storing them in linseed oil or under water. After a while, however, the resulting green colour of the liquid indicated that the process was not prevented, and the method was later rebutted by Francis Bather, Keeper of Geology at the BM(NH), in *The Preparation and Preservation of Fossils* (1908), which was possibly the first publication related to the treatment of pyrite oxidation within a museum context.

Bather's proposed treatment for deteriorating pyritic fossil collections was based on neutralising all acidic by-products caused by the reaction without harming the specimen or its matrix. He advised that specimens should be immersed in a hot solution of caustic alkali, causing in some cases a "white coating" on the specimen, which could be removed with hydrochloric acid but then must be rinsed carefully with distilled water (Bather 1908). The specimen would then be dried by passing through alcohol or petrol, and finally coated in shellac (resin from a female lac bug), or melted paraffin wax (Figure 1).

Frederick Bannister (1933), Keeper of Mineralogy at the BM(NH), developed Bather's earlier method by specifying ammonia as the key neutralising agent. Firstly, he highlighted the necessity to remove all decomposition products from the surface of the specimen, before washing under running water then immersing in an ammonia solution of 17:1 water to ammonia. The next step was to place specimens in a bath of alcohol before drying in an oven at 70°C. The specimen would finally be coated, provided the surface was confirmed acid free after testing with litmus paper (Bannister 1933). Bannister's method differed according to the specimens' stage of decomposition. For instance, rather than fully immersing fragile and severely deteriorating specimens, they were instead "suspended above a trough of strong ammonia vapour for 12 hours or more" (Bannister 1933). After rinsing with alcohol, specimens were then washed twice with acetone and allowed to drain thoroughly.

The above treatment was applied to over 250 pyritic specimens in the BM(NH) at various stages of decomposition, and of which only three were recorded as "incurable" because of continuous decomposition even after coating. Despite these encouraging results, Bannister did not define the above methods as a "permanent cure", but rather a means to "extend the life of many specimens and decrease the effects of their corrosive decomposition" (Bannister 1933).

Bannister updated his method in 1943 with the help of Miss Jessie M. Sweet, a Scientific Assistant at the BM(NH), who contributed towards the treatment of pyritic specimens. Sweet noticed that a damp atmosphere increased the rate of the oxidation reaction, and therefore advised that pyrite should never be washed with water or treated with acid (Bannister and Sweet 1943). The Mineralogy department at the BM(NH) henceforth employed just the ammonia gas treatment instead of full immersion in solution, followed by drying at 70oC without the use of alcohol, and finally coating with vinyl acetate (Bannister and Sweet 1943) (Figure 2).

Treatments for large specimens

Arthur Rixon, Experimental Officer at the BM(NH), like Bannister, maintained that there was no effective "cure" for the problem of pyrite decomposition, but only treatments that can "arrest the progress of decomposition for several years" (Rixon 1976). In particular, Rixon was referring to ammonia gas treatment for small and fragile specimens, and morpholine in alcohol which was a treatment reserved for specimens too large to fit in a treatment chamber. The latter method involved a 5% (v/v) solution of morpholine in alcohol applied as a paste over the specimen and matrix then left to dry for several hours. The process was repeated twice before the specimen was coated with a plastic varnish such as

Figure 1. Ammonite (NHMUK PI C 14397) with labels describing the treatment applied to the specimen in February 1913: "this ammonite has been boiled in a strong solution of common soda, then soaked in benzol, afterwards impregnated with paraffin wax".

polybutyl methacrylate (Bedacryl) or polyvinyl acetate in toluene. Like Bannister, Rixon also insisted on removing all decomposition products from the specimens prior to both treatment methods (Rixon 1976). Morpholine in alcohol was considered effective but it was restricted by several factors, not least the high toxicity of morpholine, its capacity to dissolve some consolidants and its hygroscopic nature, which was a particular hindrance when applying the substance because the ambient relative humidity needed to be low enough to avoid exacerbating the reaction (Howie 1977 b).

A comparatively less toxic and less damaging alternative for the treatment of large specimens is the application of ethanolamine thioglycollate (ET), which removes acidic pyrite oxidation products by reacting with them in solution (Cornish and Doyle 1984). This method was used to treat several large marine reptiles as part of the Gallery 30 Project at the NHM (see Cornish *et al.* 1995). Similar to morpholine, a paste poultice is applied to the specimen in a 5% solution of ET in alcohol, with added sepiolite to provide thickness. The substance is then left underneath polythene sheeting to avoid evaporation, and reapplied every four hours until no mauve colour is visible; this indicates that the acid has been neutralised. The area on the specimen is subsequently cleaned with another poultice of 95% IMS in sepiolite (Cornish *et al.* 1995).

Bacteria theory

A different approach towards remedial treatments came about after a theory took root in the mid-1950s, which claimed that bacteria could play a potential role in the oxidation process (Howie 1977 a). This theory was based on the discovery that a microorganism (*Acidithiobacillus ferrooxidans*, previously named *Thiobacillus ferro-oxidans*) could oxidise ferrous iron to ferric (Leathen and Madison 1949). Soon after, several workers at the BM(NH) suspected that these bacteria might be related to the deterioration of museum specimens. Experimental antibacterial treatments were conducted at the BM(NH) from circa

Figure 2. Ammonite (NHMUK PI C 6110 b) with labels describing the treatment applied to the specimen in June 1950: "treated for decomposition, with Ammonia gas and Vinyl Acetate".

Figure 3. Ammonite (NHMUK PI C 38808) with labels describing the treatment applied to the specimen in July 1972: "treated for decomposition with Morpholine and 5% Butvar containing 0.1% Centrimide".

1970, during which pyritic specimens were routinely rinsed in alcoholic solutions of 10% Savlon 10 (v/v), and later 0.1 % (w/v) Centrimide B.P., the active base of Savlon (Figures 3 and 4). These processes were applied after the then standard treatments of ammonia vapour or alcoholic morpholine. Booth and Sefton (1970) also suggested vapour phase inhibitor 4 as a solid antibacterial fumigant for use in storage and exhibition cases to control the development of thiobacteria.

After a five year period during which treated and untreated pyritic specimens at the BM(NH) underwent rigorous monitoring, Howie confirmed "the non-complicity of thiobacteria in the oxidation of pyrite in air" (Howie 1978). This was supported by multiple recorded failures of bactericidal treatments, and by results of further experimental work and observations, which contended that environmental conditions are of more importance than possible bacterial involvement (Howie 1977 b). It has since been discovered that iron oxidising bacteria requires an extremely high RH of around 95%, rarely found in museums, and it is now generally accepted that the cause of pyrite oxidation within museums is a chemical and electrochemical reaction (Buttler 1994).

The shift of focus towards RH also played an important part in the development of the ammonia vapour treatment in the 1980s. Howie advised that pyritic specimens should be stored in RH not exceeding 60% (Howie 1979), and warned that the RH above the ammonia solution could reach 70% or more which, even if the conditions are alkaline, can cause porous pyritic specimens to adsorb water vapour when exposed for the required duration (Howie

Figure 4. Fossil fish (NHMUK PV P 620) with labels describing the treatment applied to the specimen in November 1961: "treated with 10% Savlon solution Hardened with Alvar".

1979). Waller's proposed solution was the use of polyethylene glycol 400 as a humectant to reduce the high RH caused by the ammonia vapour (Waller 1987). The addition of PEG causes a depression in the water vapour pressure, thus eliminating the risk of condensation forming on specimens and keeping the RH beneath the threshold of 60% (Howie 1977 b); it is a method that is still used today as discussed in 'Project Airless'.

Evolution of oxygen barriers

After remedial treatment, appropriate storage is also vital for the preservation of pyritic specimens. In addition to his neutralisation process, Bather (1908) recommended other preventative methods to delay the deterioration of specimens on display, including the use of common washing soda as a desiccant within exhibition cases, and specimen boxes containing cotton wool above a layer of powdered chalk. The idea behind the latter method was that any sulphuric acid formed by the reaction would react with the chalk to produce carbonic acid gas instead of oxygen (Bather 1908), thereby partially eliminating a key reactant in the deterioration process. Reducing specimens' exposure to oxygen was the aim behind this technique, whereas providing a physical barrier between a specimen and the surrounding air has often been attempted in order to completely halt the oxidation process. A popular approach was to apply a coating or varnish, and these substances have often varied according to professional advice as well as the availability of materials at the time.

The earliest and most widely used coatings up until the 1930s were natural substances such as shellac (Howie 1984), which was specifically recommended by collectors during the mid-19th century as a protective barrier against air (Howie 1977 a). Other natural substances like paraffin wax were also used as consolidants to provide strength after chemical treatments, as illustrated by the ammonite in Figure 2. Bather (1908) promoted the use of shellac or nitro-cellulose ('dope') to be applied as a thin consolidant after neutralisation. Nitro-cellulose was found to be the most effective coating in a series of tests conducted by Radley (1929), during which pyritic specimens coated in various lacquers and waxes were exposed to conditions of high moisture and acidic vapours (Howie 1977 a).

Vinyl acetate appears to be the last widely used coating in the museum before a diversification of commercially available plastics in the 1950s (Howie 1984), which gave rise to a multitude of products utilising polyvinyl acetate and polybutyl methacrylate such Bedacryl 122X, the latter appearing to be particularly popular in the BM(NH) during the 1950s (Figure 5).

Although they can provide structural support and some limited protection by reducing specimen porosity (Larkin 2011), there have been misconceptions in the past that any of these coatings are completely impermeable to surrounding air, (Howie 1979; Cornish and Doyle 1984; Newman 1998), particularly when abrasions and lifting of varnish can expose areas of the specimen. In some instances sulphates will form underneath the coating causing blistering and preventing easy removal (Buttler 1994), as was the case during the cleaning and conservation of the marine fossil reptiles at the NHM (Cornish *et al.* 1995). Many of these specimens displayed signs of pyrite oxidation beneath a glossy brown coating thought to be shellac, and in order to commence conservation treatment the coating had to be removed with a solvent gel.

Decay products forming underneath oxygen-permeable coatings is a common problem for palaeontological material, and can be exacerbated when specimens are varnished with unknown substances prior to their arrival in the museum. PVA (unspecified whether polyvinyl alcohol or polyvinyl acetate) has often been used to strengthen small specimens, but sulphates can still form underneath the coating, or more likely they have been varnished over, making them particularly difficult to remove (Figure 6).

PVA also has the added disadvantage of emitting acidic vapours if applied in emulsion form (Keene 1987), a detail which would rarely be included in associated labels, and which could result in other issues such as 'Byne's disease', whereby calcium carbonate is corroded by acidic vapours (Cavallari *et al.* 2014). Nevertheless, considering the irreversible damage caused by pyrite oxidation, the use of non-conservation grade coatings has preserved the structure of many specimens that would otherwise have perished.

Liquid storage is another approach to providing oxygen barriers for small specimens, and has been utilised since the 19th century when collectors would store small specimens in inert oils, glycerol or water. We have already seen how boiling specimens and their subsequent storage in linseed oil or water was a common though ineffective technique during the 19th Century (Richardson 1842; Bather 1908). Other oils such as liquid paraffin were also most likely used up until the early 19th century (Howie 1977 a), and Rixon (1976) describes how the difficulties involved with extracting small specimens from these oils prompted the use of glycerol as an alternative storage medium, which could be rinsed away with water

Figure 5. Ammonite (NHMUK PI C 38495) with labels describing the treatment applied to the specimen in October 1957:"treated for decomposition with Ammonia gas and Bedacryl"

without the need for organic solvents. This approach, however, would not prevent oxidation due to the hygroscopic nature of glycerol, which over time would turn a dark brown colour as the iron salts within some specimens dissolved into solution (Rixon 1976; Howie 1977 a; Allington-Jones 2006).

Silicone oil was first used at the BM(NH) in the 1960s as an alternative to glycerol because, though expensive, it is inert, impermeable to air and non-hazardous. The transfer from one medium to the other, however, was not straightforward because glycerol is difficult to completely remove, and in some instances specimens thought to be thoroughly cleaned and dried when transferred to the oil were "found to be exuding globules of glycerol" two years later (Rixon 1976). Despite the importance of thoroughly drying out specimens beforehand, silicone oil has proved a useful technique for preserving small specimens to date (Collinson 1984; Newman 1998; Collinson *et al.* 2016).

Anoxic microenvironments

Oxygen barriers for larger specimens can be more problematic owing to limited storage space and the importance of accessibility. The design of the BM(NH) Palaeontology building coupled with the mixed nature of the Earth Science collections inhibits the maintenance of a low RH and temperature throughout the space (for more information see Comerford *et al.* 2008).

The ambient RH and temperature of the Palaeontology building is currently set to accommodate a range of materials as well as to provide comfortable conditions for staff working around the perimeter of the collection areas. Moreover, the majority of the Earth Science collections are organised taxonomically, therefore sub-fossil specimens containing collagen, and suited to an RH of around 50-55% (Comerford *et al.* 2008), could be housed alongside fully fossilized pyritic specimens of the same species, which should ideally be stored in con-

Figure 6. Gastropod (NHMUK PI TG 27057) with label describing treatment (date unknown): "treated with PVA". Specimen shows signs of hardened decay products on the surface.

ditions not exceeding 45%, and definitely not higher than 60% (Howie 1992; Comerford *et al.* 2008). In addition, specimens in clays and shale matrices are at risk of drying out in conditions below 30% RH, providing a tight window of between 30-45% RH for optimum storage of pyritic clay specimens.

In 2001, a large-scale microclimate was created as a short-term solution to house 300 actively oxidising fossil plant specimens (Doyle 2003). An entire collection cabinet was enclosed within a layer of Marvelseal® 470, heat-sealed along the edges and sealed to the floor with Gaffa® adhesive tape. Cassettes of Artsorb® pre-conditioned to 50% RH were placed within the cabinet as a buffer, which was low enough to reduce oxidation rates without risking damage to shale or composite specimens. The internal RH and temperature of the cabinet was monitored with a Rotronic Hygroclip® probe attached to a Meaco® 458 MHz data logger and compared to ambient conditions over a period of four months before the installation of specimens within the cabinet (for more information see Doyle 2003). The results were positive, and a similar approach was adopted to protect specimens in situ during the refurbishment of the Palaeontology building in 2002. Whole cabinets were "cocooned" within two layers of polythene sheeting sealed to the floor with hardboard between them; this provided suitable vapour barriers and microclimates for the collection while the refurbishment took place (Comerford *et al.* 2008).

Requirements for microenvironments can vary; for instance, large specimens on display like the Cranbourne meteorite require a rigid enclosure for visibility and protection. A bespoke case for the meteorite was purchased in 2008, within which the internal atmosphere is actively maintained at 0% oxygen using a nitrogen generator to displace oxygen with nitrogen gas (Allington-Jones and Collins 2011). Since there are an estimated 833,000 oxygen-sensitive pyritic palaeontology and mineralogy specimens at the NHM (Allington-Jones and Trafford 2017 a), it was considered most cost-effective and sensible for access to provide individual anoxic enclosures to prevent further decay in the long-term. Plastic containers such as polypropylene Stewart boxes containing Artsorb® or silica gel have been used at the NHM to house sensitive palaeontological specimens; this method has been largely successful in maintaining consistent RH levels, but is not suitable for providing anoxic conditions. Concerns have also been raised regarding the longevity of these plastics and the possibility of additives causing harmful emissions within a sealed environment (for more information see Larkin and Makridou 2000). Luckily, the increasing availability of low-cost barrier films and oxygen scavengers has enabled a safer, non-toxic alternative for storing specimens (Burke 1996). The NHM has been using barrier film and oxygen scavengers since the late 1990s on an ad-hoc basis and during volunteer re-storage projects, but it was not until 2015 that a large-scale conservation project was established to systematically treat and rehouse the actively deteriorating pyritic specimens within the Earth Science collections.

Project Airless: 2015 - Present

Project Airless aims to provide a comprehensive survey of all pyritic specimens within the NHM, and to treat and rehouse these specimens according to their importance and severity of decay (for more information see Allington-Jones and Trafford 2017 a). Current remedial treatments have been refined from some of the earlier methods discussed, including the removal of all decay products prior to any further treatment (Bannister 1933), by dry-brushing, followed by treatment with ammonia vapour and PEG (Waller 1987) when necessary. The standard ammonia procedure involves placing specimens within a treatment chamber along with a plastic tray containing ammonium hydroxide and PEG 400 in a 1:4 ratio, at a volume appropriate to the size of the chamber. The mixture is left within the sealed chamber for 48 hours, which is considered the optimum duration for exposure to have an effect on the specimens without risking a rise in humidity once the humectant has been exhausted. Ammonium hydroxide is both toxic and flammable, therefore it is necessary to wear safety goggles, gloves and a vapour protection mask when applying this treatment, as well as ensuring that the treatment chamber is within a fume cabinet.

Each treated specimen is stored in anoxic enclosures using Escal™ Neo barrier film (Figure 7), which comprises seven layers including a ceramic deposited polyethylene gas barrier, a protective outer layer of polypropylene, and an inner layer of polyester to allow for heat-sealing (For detailed instructions on creating anoxic microenvironments see Allington-Jones and Trafford 2017 b).

RP System® Type K oxygen scavengers are used within the enclosures; these scavengers will eliminate oxygen but not moisture, so the project team ensures that the enclosures are sealed at an ambient RH of between 40 and 50%, thereby avoiding the risk of dehydrating clay specimens as well as preventing harmful fluctuations in RH when bags are opened and re-sealed. Type A scavengers will eliminate both oxygen and moisture, and are reserved for moisture-sensitive mineral specimens.

Figure 7. Typical enclosure for small - medium sized specimens. See 'Materials List' for products used.

Internal monitoring systems such as O2xyDots® have been used in the past to detect oxygen levels within enclosures. The dots contain ruthenium dye which, under blue LED light, gives off a fluorescence that can be measured for oxygen levels by a hand-held spectrometer (Allington-Jones and Collins 2011), although all the enclosures that were confirmed to be working had a consistently vacuum-packed appearance, thus justifying a simple visual check as an appropriate monitoring system. It is worth emphasising the importance of regular monitoring after the project ends to ensure that the enclosures remain effective, and to ascertain when the barrier film needs replacing, since each barrier film has a natural lifespan dependant on its oxygen transmission rate (Burke 1996).

Figure 8. Pliosaur pubis (PV R 8322 d) on its original polyurethane support.

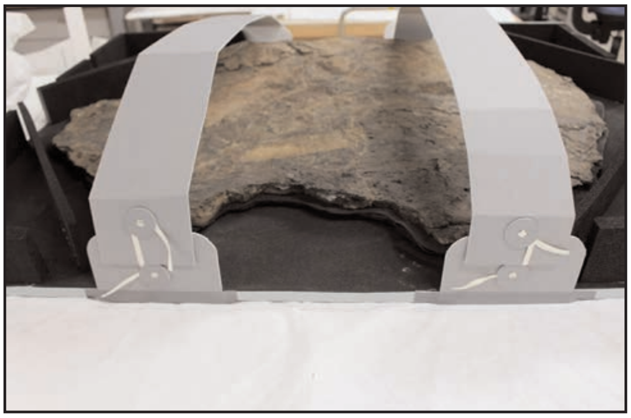

Figure 9. Easily removable card straps to protect the pliosaur pubis when enclosed in barrier film.

Systematic treatment and re-storage is not always possible when specimens are oversize or awkwardly shaped, such as the pliosaur pubis in Figure 8. Luckily this specimen was not attached to its original polyurethane support, so it could be removed using straps and plenty of padding, then thoroughly dry-cleaned with an air hose under extraction.

The original support was replaced with a jacket made from Epopast 400, an epoxy resin/glass fibre paste, upon which Plastazote®, a nitrogen expanded polyethylene foam, was used to secure vulnerable edges and to provide pockets in which to place oxygen scavenging sachets. Arches were also made from acid free card to protect the specimen from the barrier film within the enclosure, and fastened loosely at the base so they could be easily removed for future access (Figure 9).

The pliosaur pubis was too large to be treated with ammonia, and since ET was unavailable at the time, treatment for this specimen involved dry-cleaning with an air hose followed by rehousing in anoxia, although according to the conservation records it also underwent unspecified pyrite treatment in 1971.

Conclusion and further research

The Airless Project has been in progress for only four years to date, but so far over 8,600 specimens have been treated, rehoused and enriched with a digital record including images, condition assessments and treatment details. These data can therefore be utilised by future research projects to assess the effectiveness and longevity of current treatment methods, and contribute towards the developing body of research around pyrite oxidation.

Investigating historical treatments of pyrite oxidation has shown that the intentions behind each method are similar, be it neutralising acidic by-products or preventing the reaction from occurring, despite approaches varying over time in line with scientific advancement and availability of materials. This necessitates regularly reviewing current procedures and sharing knowledge across institutions to establish new and innovative ways in which to combat this problem.

Current research at the NHM includes a series of tests to establish a standard treatment for labels contaminated by the products of pyrite oxidation, and CT scanning of specimens stored within micro-environments of varying relative humidity and oxygen levels to assess changes over time in internal structure and surface differences. Scans of the same specimens will be compared over a one to two year period.

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Materials List

ESCAL™ Neo gas-barrier film (transparent ceramic) by Mitsubishi Gas Chemicals, with inner layer of heat-sealable polyester

Marvelseal® gas-barrier film (foil based film for larger/ heavier specimens)

RP System® (Type K) oxygen scavenging sachets by Mitsubishi Gas Chemicals

Double-sided tape - 3M #415

Melinex®(Transparent polyester film used as label sleeves)

Plastazote® LD45

Acid-free trays (1300 micron grey/white boxboard covered with Argentia 120gsm acid-free paper, neutral pH EVA adhesive)

Perspex templates or templates made from corrugated museum blue board corresponding to each storage tray size

Criss Cross remote heat sealer/ Cross Weld

UK AND IRISH LOCATIONS FROM WHICH GEOLOGICAL OR PALAEONTOLOGICAL SPECIMENS ARE KNOWN TO BE PRONE TO PYRITE OXIDATION

by Nigel R. Larkin[1], Caroline J. Buttler[2] and Kieran Miles[3].

Larkin, N.R., Buttler, C.J. and Miles, K. 2019. UK and Irish locations from which geological or palaeontologcal specimens are known to be prone to pyrite oxidation. *The Geological Curator* 11 (1): 19-26.

Pyrite oxidation (or pyrite decay) has been a problem in museum collections for many years. The damage to specimens can include total loss of the object and its label. There is no cure: the changes cannot be reversed but the process can be halted. Preventing pyrite oxidation in the first place is obviously preferable but maintaining the appropriate environmental conditions in a large storage area can be very difficult to achieve and monitoring the whole collection regularly for signs of pyrite decay may not be practicable. Therefore it would be useful for curators to know which specimens in their collection are most likely to suffer from pyrite decay.

Whilst there is a great deal of literature published on the mechanisms of pyrite oxidation and its treatment, there has been very little describing which sorts of specimens are prone to the process. A list of sites in the UK and Ireland from which problematic material is known is presented, with indications of what specimens from these sites are likely to suffer the most. This data has been crowd-sourced from curators, conservators, collectors and enthusiasts from around the UK and further afield. It is not definitive but is a starting point and can be added to over time.

The most important specimens from sites identified on this list can be stored in appropriate environmental conditions and/or regularly monitored. They can also be digitally imaged or physically replicated through casting or 3D printing to preserve a record in case the worst should happen in the future.

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Introduction

Pyrite oxidation (also known as pyrite decay, pyrite rot and pyrite disease) has long been known to be a problem in museum collections. Its deleterious effects on geological and palaeontological specimens are well documented (e.g. Bannister 1933; Temple and Colmer 1951; Rixon 1976; Cornish and Doyle 1984; Birker and Kaylor 1986; Cornish 1987; Buttler 1994; Cornish et al 1995; Costalgiola *et al.* 1997; Andrew 1999; Kelly and Wood 2000; Shinya and Bergwall 2007; Larkin 2011). Even valuable type specimens are not immune (Turner 1980). It is not just fossils that are affected, specimens in mineral collections are also at risk including pyrite, chalcopyrite and marcasite (Bannister 1993). Mineral specimens of pyrite may be less prone to decay than fossils, possibly because the pyrite in fossils is finely disseminated through the rock and is usually made up of many tiny spheres increasing the surface area that is exposed to unsuitable conditions (pers. comm. Mike Horne). However, even specimens such as cubic pyrite without obvious signs of decay may have microscopic evidence of deterioration. Finely disseminated pyrite or marcasite in ore minerals can be very susceptible to decay and it may be that certain crystal structures of pyrite (e.g. framboidal pyrite) are more prone to decay than others (Howie 1992). The chemical bonding and charged state of the mineral on an ion / atom level may be a factor (pers. comm. A. Hellemond). It could be that decay has been more recognised in palaeontology collections which are generally larger and possibly more frequently studied than mineral collections. Antiquities carved from stone (e.g. statues, mace heads etc) in archaeological collections can also suffer from the problem (Oddy 1977).

If left unchecked the decay process can completely destroy specimens and even their labels, which makes it difficult to know what has been lost. If the process continues for some time, entire drawers of specimens can be lost and the acidic by-products of the oxidation process have been known to chemically corrode through the base of wooden drawers and to drop onto specimens in the drawer below. Remedial action can be taken to halt the decay process in museum specimens and neutralise the acidity of the material when an affected item is discovered (Cornish and Doyle 1984; Waller 1987; Leiggi and May 1994; Cornish *et al.* 1995; Andrew 1999; Larkin 2011) and their damaged labels can be treated (Stooshnov and Buttler 2001). However, the physically damaging effects that have taken place - such as cracking, expansion and loss of surface detail - cannot be reversed. Prevention is therefore infinitely preferable to cure.

Prevention requires environmental control in the collection or display area that does not allow relative humidity (RH) to rise above 60%. However for specimens containing large amounts of organic carbon it is necessary to store them at lower than 30% RH to inhibit pyrite decay (Newman 1998). Alternatively anoxic micro-environments (Carrio & Stevenson 2002) can be created to store specimens. Attempting to maintain the appropriate environmental conditions would ideally be combined with regular monitoring programme. Although this can be difficult to achieve when the collection size is very large and/or the number of curatorial and conservation staff is small, targeted surveys are essential. It cannot be assumed that heating, ventilation and air conditioning systems are performing as well as they should be and conditions within stores can vary greatly: outside walls are cooler than inside walls (with associated higher RH) and possibly the reverse in summer if south-facing in the Northern Hemisphere; there can be stratification of temperature in the air column (and therefore associated stratification of RH); unlagged hot water pipes under floors and in walls create warm spots; and there are often cool drafts, damp spots etc. (Larkin 2013). Also, accidents happen - accidents that you may not be aware of until far too late e.g. slowly leaking pipes, or gutters, downpipes and water pipes blocked or disrupted due to building activities (Cornish *et al.* 1995; Andrew 1999).

Checking the whole collection regularly requires staff time and maintaining suitable environmental conditions in the whole storage area can be very difficult. Therefore it would be useful for curators to know which specimens in their collection are most likely to suffer from pyrite decay so that they can monitor these items in particular. They could also choose to store material likely to experience pyrite decay issues in appropriate RH conditions using silica gel or ArtSorb etc. in suitable enclosures (Larkin *et al.* 1998; Larkin *et al.* 2000), or by securely encapsulating specimens with oxygen absorbers/scavengers (Carrió and Stevenson 2002). Even whole cabinets can be encapsulated to provide suitably low RH or low oxygen conditions that should prevent pyrite from oxidising (Doyle 2003) or reduce the decay to a slower rate.

At a time when sustainability is a major goal for museums the knowledge of which parts of a collection are susceptible to pyrite decay means that time, money and energy could be saved compared to trying to reduce the RH levels in a whole collection. Whilst there is literature on the mechanisms of pyrite oxidation and how affected specimens can be treated, there has been very little published describing which sorts of specimens are susceptible. These are usually either vague descriptions such as "*Fossils from the Lias, Gault and London Clay are prone to the problem*" (Rixon 1976) or the very occasional specific reference to a single location such as "*Some of the decay appears to be collection site specific; in particular pyrite decay on specimens where the support matrix contained finely disseminated iron pyrites or chalcopyrite, an example being the calcite specimens from Wheal Wray mine*" (Ratcliffe and Valentine-Baars 2011). A guide listing locations or particular stratigraphic units that are known to yield specimens likely to be problematic if storage conditions are less than ideal would be useful to museum staff.

It is impossible to provide a definitive list because palaeontologists and geologists understand that material from exactly the same deposit will have oxidised in some collections with unsuitable environments but will have remained fine in collections with better environments, so peoples' experiences will differ. Also, specimens from within a specific small stratigraphic unit can vary in how they respond to poor environmental conditions due to the exact spot they are preserved in the unit affecting the amount of pyrite and organic carbon present in the specimen. There are other factors such as the weathering conditions at the collection site (i.e. how saturated the ground was), storage conditions immediately after collection, treatment of the specimen (fragile shale specimens have been set in plaster which can create a humid microclimate around them) and even - in the case of fossils - the genus of the specimen potentially affecting pyrite microstructure (Hodgkinson and Martin 2004).

A list of such sites in the UK and Ireland is presented below (Table 1). This was compiled from the experiences of the authors and, importantly, from responses to emails that were sent to members of the Geological Curators Group (GCG) and the Natural Sciences Collections Association (NatSCA) requesting information about material that has suffered extensively from pyrite decay in the past. It also includes information gathered from comments posted on MinDat.org (the world's largest open database of minerals, rocks, meteorites and the localities they come from). We acknowledge that it is not a comprehensive list but we consider it to be a valuable starting point in documenting where pyrite decay is likely to be found in a museum collection especially for non-specialist curators having to look after geological collections and specialist curators beginning their careers.

Discussion

Detailed data and anecdotal evidence was received from many people responding to our call for information (via GCG, NatSCA and MinDat) but not all the information could be captured in the necessarily simple list presented in Table 1 and some responses were useful but did not provide detailed information. Material from some of the Oxford Clay exposures which is very prone to pyrite decay appears several times on the list. However it is within the various shell beds that the issue is most extreme: shell beds 16 and 19 for instance contain marine reptile elements heavily encrusted with 2cm thick pyrite which starts breaking down immediately once it is collected. However fossils from the higher levels within the lower Oxford Clay at Peterborough seldom show signs of pyrite decay or even pyrite (including the large ammonites such as *Erymnoceras* sp. (Hyatt 1900)). Specimens of Pennsylvanian age (Late Carboniferous) crop up in many reports but the extent of the pyrite decay is not quantified. It may not be a major issue but appears widespread.

If particularly important material (such as a type specimen) is considered likely to be susceptible to decay based on past experience or because it is from one of the sites listed above, it should be recorded in as much detail as possible as soon as possible. In the past this would have been restricted to taking high-resolution photographs and/or taking high quality moulds of specimens and making casts, appropriately painted (Baars 2013). However, specimens can now be recorded in three dimensions in very high detail quite easily using CT scanning, Micro CT scanning, laser scanning or photogrammetry techniques depending on the availability of skills, equipment and/or funding. The data generated can be used to build digital 3D models and, if required, these can be 3D printed. These techniques have advantages over traditional moulding and casting in that they are far less invasive and should cause no damage to a fragile specimen.

Conclusions

Countless mineral and fossil specimens have been completely lost in museums the past, often along with their associated data, due to pyrite oxidation/decay. This is a problem that persists and the processes still need to be better understood.

The oxidation process can usually be prevented through storage in low RH or low oxygen conditions. This is difficult to apply on a large scale for whole collections so at-risk specimens should be identified, recorded as thoroughly as possible, and stored in suitable media that provides a low RH or low oxygen micro environment. Such preventive measures do not cost much if they are undertaken only for material most prone to the problem. In fact if material thought to be susceptible to pyrite decay is stored together in a few small, appropriately low RH or anoxic microclimates then the environment of the whole collections area may not need to be maintained within quite such a narrow band of RH. Less energy for heating, ventilation and air conditioning (HVAC) would then be required to maintain the less prescriptive conditions, therefore saving money and ultimately reducing carbon emissions (NMDC 2009).

Identifying specimens at risk from pyrite oxidation is not easy as there are so many variables that might put a specimen at risk. However, the list of sites presented here that is based on the combined experiences of many people who have worked with geological collections for many years is a starting point for identifying what British and Irish material in a geological collection might be most prone to suffering from decay. This data could be a starting point for an online database that would continue to benefit from the contributions of curators, paleontologists, mineralogists and citizen scientists over the years, providing valuable information for researchers, collectors and curators. It need not be restricted to locations within the UK and much more detail could be added on the geographical locations and lithostratigraphical units involved. It is hoped that a suitable organisation or institution can be found to host such a database.

County	**Place**	**Stratigraphy**	**Affected specimens**
Bedfordshire		Lower Greensand Formation, especially the Woburn Sands (Cretaceous)	Wood
Bedfordshire	Stewartby	Oxford Clay	Marine reptiles
Buckinghamshire	Woodham [Brick-pit]; Calvert [London Brick Co. Pit]; [Newton Longville Pit], Bletchley; Bierton	Lower Oxford Clay and Upper Kimmeridge Clay (Jurassic) & Oxford Clay. Athleta Zone, Callovian (Middle Jurassic)	*details not given*
Cambridgeshire	Yaxley	Oxford Clay	E.g. marine reptiles
Ceredigion	Alltycrib Mine, Tal-y-bont		Marcasite specimens
Ceredigion	Esgair Hir & Esgair Fraith mines, Tal-y-bont		Marcasite specimens
Ceredigion	Eaglebrook Mine, Ponterwyd		Marcasite specimens
Cornwall	Wheal Jane mine, Baldhu		Specimens of ludlamite with pyrite are extremely susceptible.
Cornwall	Wheal Wray mine, Moretonhampstead		Matrix susceptible
Cornwall	Perran St. George Mine, Perranporth		mineral specimens
Derbyshire	Stubben Edge Hall	Westphalia Coal Measures / Pennsylvanian (Carboniferous)	Mainly goniatites
Derbyshire	Glebe Mine, Eyam, near Bakewell	Stopes above 380 [feet] level, Ladywash section, Old Edge Vein	*details not given*
Dorset		(Lower Jurassic)	Especially ammonites
Dorset	Charmouth/Lyme Regis	pyrite beds in the Black Ven Marls (Jurassic) *Obtusum* Chronozone Belemnite stone band and the Shales with Beef (Jurassic)	Macrofossils, vertebrates, particularly around the 'Birchi' nodules
Dorset	Rope Head Lake & Cuddle, Kimmeridge	*hudlestoni* and *scitulus* Zones - Lower Cattle Ledge Shales (Jurassic)	Ammonites Specimen and matrix
Dorset	Hen Cliff, Kimmeridge Ledges, Kimmeridge	*elegans* biozone Hen Cliff Shales [Formation] (Jurassic)	Ammonites Specimen and matrix

Table 1 Locations in the UK and Ireland known to yield fossil and mineral specimens that are particularly susceptible to pyrite decay, listed alphabetically by county. Some spaces remain blank as detailed information was not always given by contributors; some places are regions or counties rather than specific locations.

Dorset	Charmouth/Lyme Regis Stonebarrow	Charmouth Mudstone Formation (Jurassic)	Most pyritised macrofossils
Dorset	Ham Cliff, Red Cliff Point, Weymouth, Dorset	Oxford Clay. *Quenstedtoceras lamberti* Zone, Callovian (Upper Jurassic)	Ammonites
Durham	Groverake Mine, Rookhope, near Stanhope		*details not given*
East Midlands		Lower Oxford Clay (Jurassic)	Most pyritised macrofossils
Gloucestershire	Hampstead Farm Quarry, Chipping Sodbury		Particularly iron sulphide / marcasite
Gloucestershire	Westbury on Severn	Rhaetic Bone bed (Triassic)	*details not given*
Dorset/ Hampshire	Between Highcliffe, Dorset, and Barton on Sea, Hampshire	Barton Group, Notably from Burton's beds B-G, Bartonian, (Eocene)	Gastropods, bivalves
Hampshire	Gosport	Bracklesham group (Eocene)	*Details not given*
Herefordshire	Ledbury	Ludlow (Silurian)	Macrofossils
Isle of Wight		Wealden Group: Vectis Formation (Cretaceous)	Pyritised vertebrate material
Isle of Wight		Wealden Group: Wessex Formation plant debris beds (Cretaceous)	Wood
Isle of Wight	Brook Bay	Wealden: (Cretaceous)	Matrix of dinosaur bones
Kent	Hastings	Wealden (Cretaceous)	Dinosaurs
Kent	Isle of Sheppey Warden Point	London Clay, Ypresian, (Lower Eocene)	Macrofossils including bivalves, nautiloids crustacea, fish, plants
Kent	Folkestone Paddlesworth brickpit, near Snodland,	Gault *lautus* biozone Gault Clay. *Mortoniceras inflatum* Zone, *Hysteroceras varicosum* Subzone, Upper Albian (Lower Cretaceous)	Pyritised macrofossils
Kent		Lower Chalk (Upper Cretaceous) Lower Chalk Zig Zag member	Marcasite nodules
Lancashire	Bankhall Colliery, Burnley,	Roof of Union seam, Coal Measures, Pennsylvanian (Carboniferous)	Coal balls

Lancashire		Coal Measures (Carboniferous)	Plants. In particular ‘coal balls’ - 3D plant material in large calcareous nodules that can contain significant secondary pyrite
Lincolnshire		Speeton Clay (Lower Cretaceous)	Ammonites in particular
Norfolk	Bacton	Cromer Forest Bed (Pleistocene)	Pleistocene vertebrates. Within the matrix encrusting the specimens
Northamptonshire	Aynho	Middle Lias. *Margaritatus* Zone, Upper Pliensbachian (Lower Jurassic)	Mollusca
Oxfordshire		Upper Kimmeridge Clay (Jurassic)	Most pyritised macrofossils
Oxfordshire	Wolvercote Sumertown	Oxford Clay. *Athleta* Zone, Callovian (Middle Jurassic)	Most pyritised macrofossils
Powys, Wales	Bacheiddon Mine, Machynlleth		Marcasite
Somerset	Street	Lias (Lower Jurassic)	*details not given*
Surrey	Aldbury	Gault Clay (Cretaceous)	Ammonites
Sussex		Chalk (Cretaceous)	Marcasite
Sussex	Bognor Regis	London Clay (Eocene)	Coleoptera (beetles)
Sussex	Bracklesham Bay	Bracklesham Beds / Bracklesham Group	E.g. Gastropods, bivalves, fish
Warwickshire		Charmouth Mudstone Formation (Jurassic)	Most pyritised macrofossils including ammonites
Warwickshire	Lawford near Rugby	(Pleistocene)	Mammals
Warwickshire	Fenny Compton,	Lower Lias. Lower Jurassic	Brachiopods
Wiltshire	Iles Pit, side of railway, south of Stratton St. Margaret, near Swindon,	Kimmeridge Clay Kimmeridgian (Upper Jurassic)	Ichthyosaurs
Yorkshire		Coal Measures (Carboniferous)	‘Coal balls’ - 3D plant material in large calcareous nodules that can contain significant secondary pyrite
Yorkshire		Coastal localities such as Whitby, Runswick Bay, Kettleness and Staithes (Jurassic)	Pyritized/partially pyritized fossils, especially plant material

Yorkshire	Reighton Gap	Speeton Clay (Cretaceous)	Ammonites, marine reptiles
Ireland	Knockanroe Mine, Silvermines, near Nenagh, County Tipperary		Pyrite, sphalerite and galena
Ireland	Tynagh mine, near Portumna, County Galway		*Details not given*
Ireland	‘all the great Irish zinc mines’ e.g. Tara in County Neath and Galmoy, in County Kilkenny		Framboidal pyrite
Ireland	Keel, near Longford, Co. Longford		*Details not given*
Ireland	Jarrow, County Kilkenny	Westphalian A / Pennsylvanian (Carboniferous)	Amphibians and fish

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COUNTING THE COSTS (OF LOW-OXYGEN STORAGE PROJECTS)

by Lu Allington-Jones

Allington-Jones, L. 2019. Counting the costs (of low-oxygen storage projects). *The Geological Curator* 11 (1): 27-31.

The cost in damage caused to earth science collections by pyrite oxidation is well known. But what are the costs of re-housing specimens in low-oxygen microenvironments? This article explores the financial, temporal and spatial costs of a re-storage project, in an attempt to aid collections management planning.

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Introduction

According to current knowledge, low-oxygen microenvironments are the most effective method for preserving pyritic material (Allington-Jones and Trafford, 2017) and also certain types of meteorite, polymers (Dyer et al., 2011) and organic material such as works of art on paper (Lerwill et al., 2015; Tate, 2012). Large-scale storage projects have been undertaken by several museums in recent years (e.g. Hay 2018; Teare and Measday 2018; Trafford and Allington-Jones, 2016) and this article outlines the costs involved, and the additional aspects to consider, when planning a low-oxygen re-storage project. This focusses on pyritic fossil material, but most of the considerations are applicable to other types of collection.

Techniques and materials mentioned within this article follow recommendations by Trafford and Allington-Jones (2017), with specimens re-housed in hand-cut polyethylene nitrogen expanded foam cushions (e.g. Plastazote®), acid-free trays, polyester pockets for labels and ESCAL Neo barrier film enclosures with RP System® oxygen scavengers, but there are other systems available. Examples of costs are reported using three differing sizes of fossil specimens (an ammonite, a fish on a matrix block and a plesiosaur limb bone). Their dimensions are shown in Table 1. In theory, these examples can be used to extrapolate the costs for a large collection, once numbers and object sizes have been estimated. The costs are accurate at the time of publication and based on bulk-buying from distributors. For all types of cost, it is always good practice to also include a certain amount of contingency for unseen risks such as an increase in price of cardboard, or a computer malfunction causing delays.

Temporal costs

The initial step in costing out a project would be to survey the collection and prioritise the specimens requiring re-storage, whether choosing all specimens from potentially pyritic horizons or just those with severe and active deterioration, or simply focusing on only Type and figured material. The times stated in Table.2 include the time taken to make a tray, place one label in a polyester pocket and attach this to the side of the tray, cut the 2mm and 10mm foam, construct a microenvironment enclosure and seal it with the appropriate scavengers. This time can be reduced by purchasing pre-made trays. The increase in financial cost would be slightly offset by a reduction in cost of staff time (and therefore wages), which would depend on salary levels. As long as equipment and materials are to hand, a tray only takes a few minutes to make but even a small pre-made tray can cost £1.50 (50p per minute would be a very high wage). The time taken to make enclosures for a series of standard-sized trays can be reduced by using a cross-shaped Perspex template as a direct cutting guide on the barrier film.

Example	Dimensions (mm)	Enclosure type
Ammonite	45 x 40 x 15	Apical aperture (Fig.1)
Fish on matrix block	160 x110 x 50	Apical aperture (Fig.1)
Plesiosaur limb bone	540 x 240 x 65	Lateral aperture (Fig.2)

Table 1. The three types of fossil used as examples throughout this article.

Figure 1. Apical aperture (or gift-style) enclosure, produces a minimal increase in footprint.

Figure 2. Lateral aperture (or pillow-style) enclosure, which is suitable for specimens with proportionately low height.

Example	Time (minutes)
Ammonite	10
Fish	12
Limb bone	8

Table 2. Temporal costs of physical re-storage by an experienced person (this should be doubled for a trainee).

The time taken to physically re-store each specimen is low, and does not differ greatly between specimen sizes. The greatest time required to process each specimen will be taken completing condition reports, digital photographs, and any remedial treatments required. These will vary greatly depending on the project and the resources available. It is therefore important to decide on the complexity level for condition reports: a simple spreadsheet to record oxidation and cracking, or full reports describing the exact nature and location of deterioration. To include these in estimates, the best method would be to record the time taken to undertake a chosen approach and add it to the re-storage time before extrapolating to the size of the collection.

The survey undertaken before project inception can also include estimates of remedial conservation requirements. The level of remedial conservation chosen will have a significant impact on time: dry cleaning, ammonia vapour treatment (Irving 2001) or ethanolamine thioglycollate paste or immersion (Cornish and Doyle 1983), repairs, and label conservation. These will have an additional effect on time where writing treatment proposals, recording treatments and taking post-treatment images is required.

Other time-consuming matters to consider include staff training, initial set up of the work area, surveying the collections, ordering materials, liaising with collections managers, transferring specimens between the collections storage area and the laboratory, and finding new locations for specimens which no longer fit into their storage drawer. Of course, staff time can be significantly reduced by setting up a volunteer project, and deciding on their level of involvement (whether just making trays and enclosures, or undertaking condition reports and treatments as well).

Financial costs

Table 3 can be used to estimate costs by extrapolation, according to the number of each size of specimen in your collection. The greatest costs pertain to the oxygen scavenging sachets.

	Escal Neo barrier film	Plastazote foam 2mm thickness	Plastazote foam 10mm thickness	Cardboard for tray	RPK oxygen scavenger	Total Price in 2018
Ammonite	£1.51	£0.01	£0.02	£0.07	£0.84	£2.45
Fish	£6.05	£0.04	£0.16	£0.86	£2.52	£9.63
Limb bone	£5.08	£0.27	£1.15	£1.80	£38.29	£46.59

Table 3. Financial costs for enclosures at the time of publication. Plastazote costs are based on 2m x 1m sheets, Escal™ Neo on 100m x 1m roll and card on 1.64m x 2.45m sheets. The cross-shaped net of the apical aperture style bags were tessellated to use less barrier film. The apical aperture bags were quite generously sized to allow for repeat opening and reseal when specimens are required for research or exhibition.

Trays can be constructed from acid-free fluted boxboard and either sewn with binder's thread or secured with nickel-plated rivets. Additional costs entail the cost of rivets at £19.00 for 100, double sided tape £10.50 for 33m, and label sleeves £4.38 for 100. Tools required comprise a safety ruler, binder's thread, needle, awl, heat-sealer, scalpel and knife blades, bone folder, calculator, pencils and erasers. Pre-made trays (acid-free archival boxboard covered with acid-free paper and adhered using neutral pH EVA), would cause an increase in financial cost by £1 - 4 per specimen.

Depending on the level of intervention chosen, cleaning brushes, ethanolamine thioglycollate and ethanol, ammonium hydroxide and PEG 400, camera, adhesive and consolidant (such as Paraloid B72), acetone and syringes will also be required. A decision will need to be made on the value of including oxygen indicators. Ageless Eyes® have been found to lose functionality after a period of approximately 6 months if unrefrigerated, so are unsuitable for long-term storage. Fluorescing indicators such as O2xyDots®, can prove very expensive because a specialised machine must be purchased to read them. Usually the integrity of enclosures can be judged visually, a sucked-in appearance means the barrier and scavengers are working, but a puffed appearance implies that the seals have been compromised or the scavengers expended (Allington-Jones and Trafford 2017).

Spatial costs

The majority of expansion in space will be created by the trays and foam supports, rather than the low-oxygen enclosure itself. If specimens were previously stacked on top of each other (Figure 3), this will cause the greatest expansion in space. Apical aperture bags create a smaller increase in footprint than lateral aperture bags, for example a lateral aperture bag for an ammonite would cause a 300% increase in footprint, compared with 78% increase for an apical aperture bag. Lateral aperture enclosures are, however, more economical on barrier film, and are most appropriate for specimens of low height in relation to their length and width. There are several techniques to try to minimise the increase in space created, for example extremely small specimens could be incorporated into one enclosure (Figure 4), whilst large multipart specimens can be stored in double- or triple-layered trays within the primary tray (Figure 5). The air must be squeezed from the top of all bags before sealing, to ensure that an excess increase in volume is avoided.

Figure 3. These oxidising ammonites are extremely crowded. Adding foam surrounds will considerably increase the amount of storage space required.

Figure 4. To address spatial considerations, these Eocene beetles (only a few millimeters in length) have been stored in glass vials within a polypropylene grid.

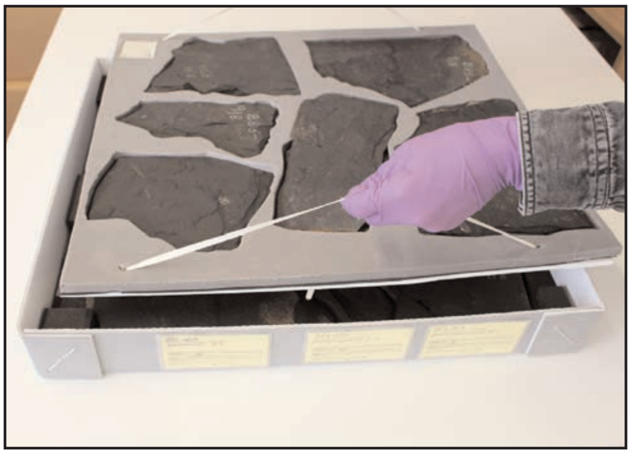

Figure 5. Reducing the potential increase in footprint of multipart specimens can be achieved by constructing trays with multiple decks.

1a. Ammonite with no existing tray Specimen size: 45 x 40mm = 1800mm^2 Enclosure size: 80 x 80mm = 6400mm^2 **Percentage increase in footprint: 155%**	**1b. Ammonite with existing tray** Tray size: 60 x 60mm = 3600mm^2 Enclosure size: 80 x 80mm = 6400mm^2 **Percentage increase in footprint: 78%**
2a. Fish with no existing tray Specimen size: 160 x 110mm = 17600mm^2 Enclosure size: 210 x 140mm = 29400mm^2 **Percentage increase in footprint: 60%**	**2b. Fish with existing tray** Tray size: 190 x 130mm = 24700mm^2 Enclosure size: 210 x 140mm = 294000mm^2 **Percentage increase in footprint: 19%**
3a. Limb bone with no existing tray Specimen size: 540 x 240mm = 129600mm^2 Enclosure size: 650 x 300mm = 195000mm^2 **Percentage increase in footprint: 50%**	**3b. Limb bone with existing tray** Tray size: 580 x 280mm = 162400mm^2 Enclosure size: 650 x 300mm = 195000mm^2 **Percentage increase in footprint: 20%**

Table 4. Examples of expected foot-print increase of specimens with and without an existing tray and foam surround.

Table 4 shows examples of the expected foot-print increase of specimens with and without an existing tray and foam surround. The increase is unsurprisingly far greater if the specimens are crammed together without their own trays. In these examples, there is a lower percentage spatial increase for fish than for ammonites because the size of the scavengers and width of the edge-seal stay the same, regardless of specimen size.

Future costs

Unfortunately low-oxygen storage also has long-term costs which require consideration. When enclosures are opened for research and display, the scavenging sachets will need to be replaced, taking up additional staff time and financial costs. Communication with researchers and collection managers is essential so that the enclosures are carefully opened in a way that will allow re-sealing, otherwise new enclosures will need to be created. Eventually bags may need to be re-made if they are opened several times or handled roughly.

Oxygen migration will continue over time (at an extremely reduced rate) through the barrier film. The scavenging sachets may need to be replenished after a period of approximately 10 years (Allington-Jones and Trafford 2017; Teare and Measday 2018). This term would be increased by adding extra sachets at the first seal, but this would almost double the initial cost, and increase wastage if enclosures are opened and re-sealed within this time. Staff time will be required for checking the state of enclosures, possibly at 5 and 10 year intervals.

Conclusion

The cost in deterioration of oxygen-sensitive material caused by inaction is well known, but the costs of undertaking a re-storage project can be daunting. With careful surveying and prioritisation, decisions can be made to focus on more significant areas of the collection or concentrate on preventive rather than remedial techniques, and so minimise the costs. A re-storage project is certainly less costly than maintaining actively controlled glass cases or an entire climate-controlled facility.

Example	Financial cost (2018)	Footprint increase	Time (minutes)
Ammonite	£2.45	78%	10
Fish	£9.63	19%	12
Limb bone	£46.59	20%	8

Table 5. A summary of all costs for the 3 example specimens in enclosures with hand-made tray, foam and scavenger (time does not include documentation).

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KEEP CALM AND CALL THE CONSERVATOR: IT IS ONLY PYRITE DECAY AND YOUR SPECIMEN MAY BE SALVAGEABLE

by Nigel R. Larkin

Larkin, N.R. 2019. Keep calm and call the conservator: it is only pyrite decay and your specimen may be salvageable. *The Geological Curator* 11 (1): 33-38.

You may discover a specimen in your collection that is suffering from pyrite decay and it may already appear to be too late to save it. However, a pile of ash-like substance in a card tray might look like it is destined only for the bin but careful cleaning and simple stabilisation techniques may reveal a useful specimen underneath. If so, record it as fully as possible as soon as possible using either traditional techniques (photography and/or moulding and casting) or by using modern techniques such as photogrammetry, CT scanning, Micro CT scanning or laser scanning as the specimen will be prone to further deterioration in the future.

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Introduction

Ideally, museum staff would be able to prevent mineral and palaeontological specimens from undergoing pyrite oxidation (also known as pyrite decay, pyrite rot and pyrite disease) in the first place by maintaining appropriate environmental conditions in the collections area and/or by using appropriate storage media to provide a suitable microclimate (Doyle 2003; Larkin 2011) for specimens most at risk. See Larkin *et al.* this volume, for a list of UK sites known to yield particularly problematic material. However, for a variety of reasons some specimens are more susceptible to pyrite decay than others. Specimens from within a specific small stratigraphic unit can vary in how they respond to poor environmental conditions due to a number of factors. This can include the exact spot they are preserved in the unit affecting the amount of pyrite and organic carbon present, weathering conditions at the collection site affecting a specimen, storage conditions immediately after collection and even - in the case of fossils - the genus of the specimen potentially affecting pyrite microstructure (Hodgkinson and Martin 2004). With luck (and, importantly, a good inspection regime) you will catch the decay in its early stages and will be able to treat it appropriately. Sometimes, however, you may be presented with what looks like the worst case scenario and will be tempted to immediately de-accession the card tray of acidic ash-like dust although you may not know which specimen it once was, as the label may be lying partly or wholly destroyed within or underneath the by-products of the decay process.

Prevention is better than cure

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. Reducing the moisture and/or oxygen around a specimen can be achieved, but at cost and inconvenience so a compromise inevitably has to be reached. Maintaining a low enough relative humidity (RH) 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). Note, however, that specimens containing large amounts of organic carbon should always be stored at less than 30% RH to inhibit pyrite decay (Newman 1998).

Unfortunately, although the environment of some museum 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, 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 - see Fenlon and Petrera 2019), or stored in desiccation chambers made of Perspex or similar material. Oxygen scavengers or absorbers can be placed within these media for further protection to reduce oxygen levels, or a desiccant (see below). 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 moisture, thereby lowering atmospheric humidity. The most common types of desiccants are silica gel (Weintraub 2002), a molecular sieve (Haynes *et al.* 2015) or preconditioned Artsorb (Doyle 2003). The ensuing RH of the sealed microclimate can be monitored with a colour-changing card also placed within the container. Usefully large lidded polypropylene containers are available (for instance 'Stewart Boxes' up to 320mm x 320mm wide by 160mm deep), but the quality of the container is of paramount importance as its 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).

Cleaning, treatment and storage of affected specimens, and recording them before future deterioration

If you do find a badly damaged specimen in your collection suffering from advanced pyrite decay you will know by the appearance (see Figs 1 to 9) and probably the smell (do not sniff the specimen itself, as that would be hazardous). Card trays, paper labels and even wooden drawers may look 'scorched' as if burnt. They have actually been burnt chemically and will be fragile. There will probably be a pile of ash-like material on the surface of the specimen. This is the acidic by-product of the oxidation process and it may smell metallic and sulphurous. The specimen may have expanded and cracked. The good news is that underneath the worrying pile of detritus from the decay process you may still have a specimen that is recoverable and useful. You - or your conservator if you are lucky enough to have one - should be able to clean the specimen using small artists paint brushes, tweezers, scalpels, wooden toothpicks and a gentle vacuum to remove the ash-like substance and any crust whilst wearing gloves, mask and googles and working in or under a dust extract if you have one. If it appears that it is the matrix that is the problem rather than the specimen itself it would be worth removing as much matrix as possible with scalpels etc and if necessary with pneumatic preparation pens. The specimen may be too fragile for cleaning with an airbrasive unit. Removal of the by-products, any crust and in particular the removal of pyritic sediment from around the fossil will reduce the chances of and/or extent of further problems with pyrite oxidising.

Ideally, after removing all the by-products of decay you would treat the damaged and fragile labels (Stooshnov and Buttler 2001) and then treat the specimen to neutralize the acidity and halt the decay process by using either the ethanolamine thioglycollate technique (Cornish 1987; Cornish and Doyle 1984) or the ammonia gas technique (Waller 1987; Andrew 1999), both of which are summarised in Larkin 2011. Unfortunately, both of these procedures require specialist equipment and experience and may be precluded by your institution's health and safety regime.

However, you can still consolidate the specimen and undertake repairs (your specimen may well be in pieces) using Paraloid B72 or a similar suitably reversible adhesive and consolidant. Then, at the very least, take good photographs of the cleaned specimen for your records as it may well deteriorate again in the future. Consider making a good mould of the specimen to preserve a record of its current morphology (Baars 2013). 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. Both the mould and cast should be accessioned and labelled. Alternatively, it costs very little to take several good digital photographs from all angles and use photogrammetry techniques to produce a digital 3D model (Larkin and Dey 2017). If funds or equipment allow, and if the specimen is worth the trouble (i.e. if it is scientifically or historically important) then consider CT scanning or MicroCT scanning the specimen or use laser scanning equipment. The data can be kept on file, or could be turned into a three-dimensional digital model which could be 3D printed if deemed necessary. Once it has been sufficiently recorded, place the specimen in a good quality ziplock polybag or in a good quality plastic (polyethylene or polypropylene) lidded container with RH-lowering Artsorb or silica gel or encapsulate it with a suitable oxygen scavenger (see above and other papers in this volume). Any of these methods should reduce the chances of the specimen suffering from decay in the future. If the specimen does deteriorate it will at least be encapsulated and therefore is less likely to affect other specimens or labels.

Examples

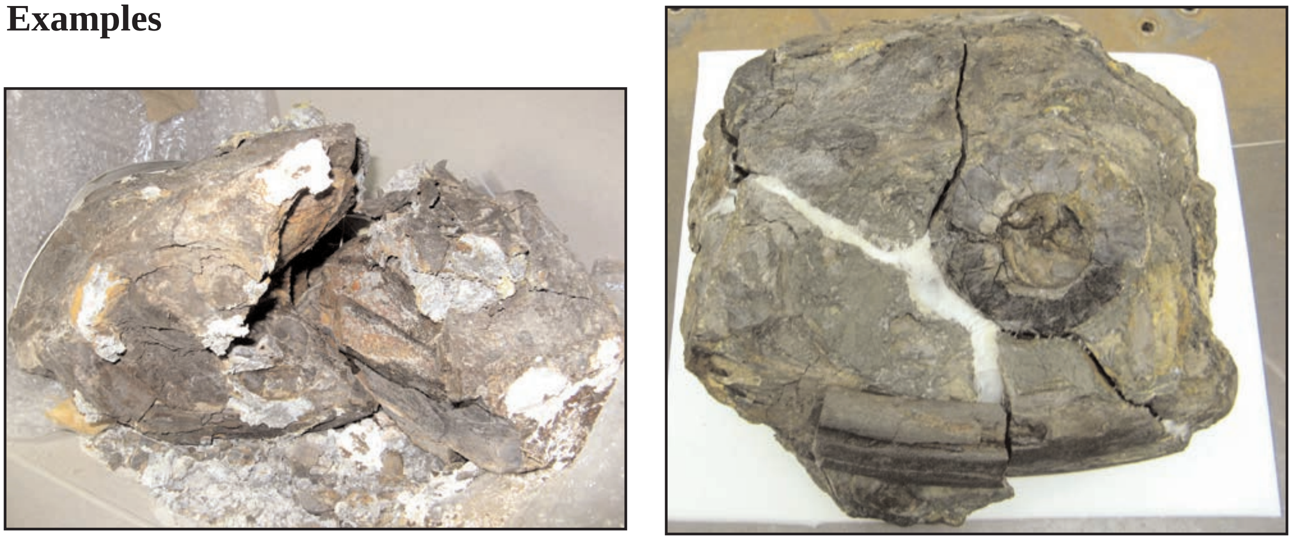

Figure 1. A large partial ichthyosaur skull. On the left as found in the collection, broken in pieces with lots of grey and white ash-like powder on the surface and a yellow crust, all symptoms of pyrite decay. On the right, after cleaning, conservation and repair. There are still gaps as the pieces of the specimen expanded and changed shape. The white area in the middle is a gap filler, and the specimen lays on a board lined with Plastazote foam.

Figure 2. A group of bivalve molluscs preserved in pyrite. On the left, covered with a layer of white and grey ash-like powder. On the right, after cleaning.

Figure 3. Small ammonites in Oxford Clay sediment. A larger ammonite on the side of the block of matrix had completely deteriorated. Note the label has been sleeved to protect it from chemical burns in the future.

Figure 4. This small ammonite looked like it had been destroyed by pyrite decay (left), but after cleaning and conservation it is still a useful specimen (right).

Figure 5. This ammonite was partially covered in a crust of white and grey powder when found in the collection (left) but was cleaned and consolidated (right).

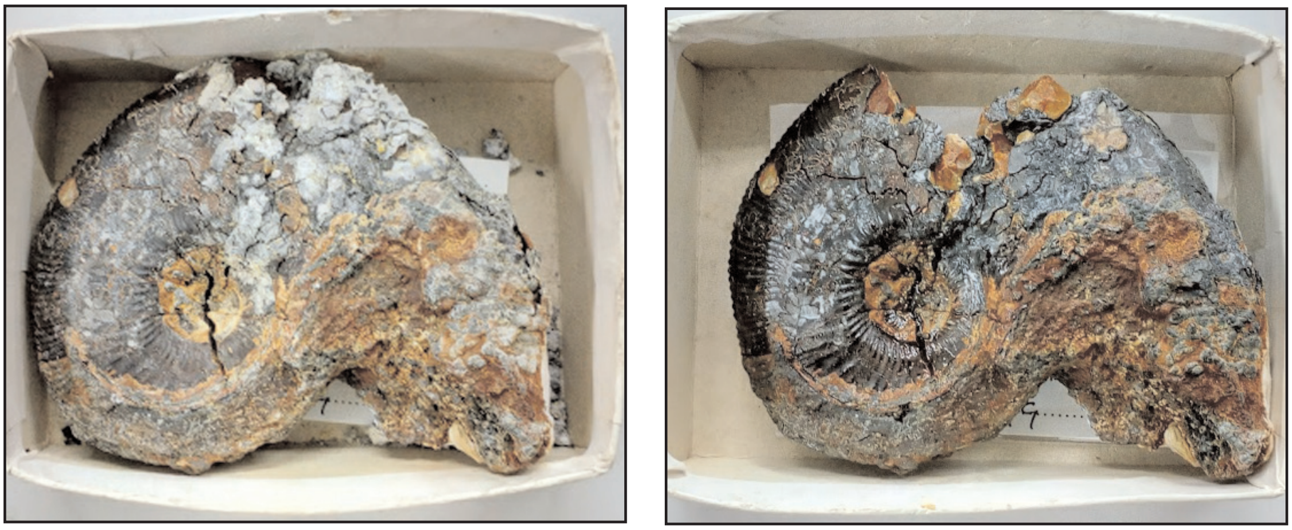

Figure 6. This ammonite was partially covered in a crust of white and grey powder when found in the collection (left) but was cleaned and consolidated (right).

Figure 7. This ammonite was almost hidden under the pile of white and grey powder by-products of pyrite decay when found in the collection (left) but after cleaning and consolidation the remaining portion still has fine surface detail (right). Note the sleeved label.

Photographs on the left (in figures 1-7 previously) show a specimen affected by advanced pyrite oxidation before cleaning, consolidation and repair. Photographs on the right (in each of the same figuresss) show the same specimen after cleaning and conservation, although the card trays have not yet been replaced in some of these images.

Conclusions

Pyrite oxidation can completely destroy specimens and their labels. The effect on a specimen of even relatively minor levels of pyrite decay can be damaging and are irreversible. However, the chances of pyrite oxidising can be greatly lowered by placing the material most at risk in suitable microclimates and there are many ways this can be achieved. A good inspection regime checking the rest of the collection regularly will ensure that any problems are spotted and treated sooner rather than later, limiting damage. If specimens are found to have deteriorated due to pyrite oxidation, do not assume that the material has to be deaccessioned and thrown away. Take appropriate health and safety measures to protect yourself and those around you and at the very least clean the specimen and check what is left under the powder. After cleaning and conserving the specimen, record it as fully as you can, bearing in mind it may soon deteriorate further. If you have the appropriate facilities neutralise the acidity using either the ethanolamine thioglycollate or ammonia gas technique. If you are not sure what to do, seek specialist help from GCG or NatSCA colleagues or from a geological conservator.

Acknowledgements

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ANOXIC STORAGE FOR 'PYRITE DECAY' AT OXFORD UNIVERSITY MUSEUM OF NATURAL HISTORY - AN EXERCISE IN COST-EFFICIENCY AS WELL AS LONG-TERM PRESERVATION

by Joy Irving and Philip Hadland

Irving, J. and Hadland, P. 2019. Anoxic storage for 'pyrite decay' at Oxford University Museum of Natural History - an exercise in cost-efficiency as well as long-term preservation. *The Geological Curator* 11 (1): 39-54.

'Pyrite decay', the oxidation and disintegration of pyrite and marcasite-bearing geological specimens, is a serious problem in many natural history collections, and is often further compounded by financial or staffing restrictions that prevent best practice being implemented. This paper explains how pyrite decay has been addressed at the Oxford University Museum of Natural History (OUMNH) in the past, and outlines a recent project to first survey the collections and then to prioritize, treat and re-store vulnerable specimens in anoxic / low humidity microclimates, in order to ensure their long-term preservation for future use. The project has been guided throughout by the need to minimize the burden on staff, reduce costs and avoid wastage, and as such is likely to have relevance for other institutions where time and resources are limited.

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Introduction

Regular monitoring of store-rooms for relative humidity (RH) and temperature have highlighted the large seasonal and daily variations which are to be found in a temperate climate in a Victorian building without internal climate control. Whilst the oak cupboards and drawers in which the specimens are stored do provide a buffer against the extremes in RH, this is not enough to prevent the onset of oxidation in vulnerable specimens. The solution is the use of micro-climates. Stewart boxes containing conditioned silica gel were the museum micro-climate storage system of choice in the 1990s. However, the problem with this type of storage has been the unsustainable, labour-intensive nature of changing the silica gel annually, as well as the difficulty of ensuring that the humidity levels in the boxes remain low enough to prevent re-oxidation. A longer-term solution was required.

The aim of a micro-climate storage system in the museum context is to extend the life of vulnerable specimens for as long as possible, in as good a condition as possible, whilst at the same time reducing the maintenance burden on staff as much as possible. What this means in practise is the long-term elimination of oxygen and / or humidity from each micro-climate. With the availability of the low transmission, transparent gas barrier film Escal, and RP oxygen-absorbing sachets, long-term anoxic storage eventually became a viable option. With finances strictly controlled and staff numbers decreasing, the following project has adhered to the above objective from the outset, whilst also bearing in mind the need to reduce costs and avoid wastage. With many museums suffering similar financial constraints, this project has relevance for others in a similar position.

The project goals were :
to uncover the extent of pyrite decay in the palaeontological collections;
to determine how many person-hours are required to measure, record and double-bag one batch of 25 specimens into anoxic storage, with the object of extrapolating to the collections as a whole;
to expand this into a one-year project to group specimens into priority categories with the object of placing as many of the high priority specimens into anoxic storage as possible;
to record actual person-hours spent on the project so far, and, assuming the same number of personnel, to predict how many months or years it will take to double-bag all known vulnerable specimens.

What is 'pyrite decay'?

The term 'pyrite decay' refers to oxidation of the minerals pyrite and marcasite, which are dimorphs of iron disulphide, FeS_2. It is caused and accelerated by the presence of oxygen and water vapour in the air. It has been postulated that sulphur-reducing bacteria may also play a role. This has been proven in the very high % RH present in mines, though not in the % RH range normally found in the museum environment. The idealized formula (after Larkin 2011) is given below, but in practice, the hydrated iron sulphate oxidation products generated will vary in composition depending on the associated minerals or the rock matrix. During pyrite decay, these oxidation products commonly appear as yellow or grey-white micro-crystalline efflorescences. They form both on the surface and within specimens, and as they occupy more space than the original pyrite or marcasite, their growth is typically accompanied by cracking and fragmentation of the specimen [see Figure 1].

$$4FeS_2 + 13O_2 + 2H_2O = 4FeSO_4 + 2H_2SO_4 + 2SO_2$$

pyrite + oxygen + water = ferrous sulphate + sulphuric acid + sulphur dioxide

The sulphuric acid not only maintains and spreads the 'decay' process, but also burns its way through labels and trays. It may also react with associated mineral species or the rock matrix. Oxidizing pyrite in a high humidity environment (> 60% RH) can also release acidic sulphur dioxide gas, which in turn can also combine with water vapour to produce sulphuric acid, further compounding the problem. A more detailed account is provided by Larkin (2011).

Pyrite and marcasite are very common in palaeontological collections, with specimens from certain horizons, i.e., clays, shales, mudstones and slates, being particularly vulnerable. Examples include the Oxford Clay, London Clay and Gault Formations. In mineral collections they occur not only as specimens in their own right, but also frequently turn up as associated species, which may not be recorded in specimen documentation. Both minerals are common in ore and petrological collections. Pyrite decay is potentially very widespread, and therefore presents a significant conservation problem in museum geological collections.

Past treatment of pyrite decay in the Museum

The management of pyrite decay in the past reflects organizational divisions in the Museum. The staffing of palaeontological and mineralogical collections was entirely separate, and holdings of petrological collections were restricted to a few historic collections until the research petrological collections and their storage areas in the Department of Earth Sciences came under Museum management in the early 2000s.

In the palaeontological collections, specimen labels from the 1960s record the use of ammonia as a treatment followed by Bedacryl (CAMEO 2018), a transparent acrylic resin, as a varnish. Savlon Hospital Concentrate (Malahyde I. S. 2018), a bactericide, was also employed as a treatment at this time, because from the 1940s to 1960s, it was believed that pyrite decay was caused by bacterial action (Howie 1992a). However, its use was limited, as it was considered to be ineffective, and being a 'thick yellow-orange liquid', it was also difficult to use (Powell 2011).

In the mineralogical collections, specimens were also soaked in Savlon. Notes found with a couple of specimens indicate that the specimens were washed several times in very hot water to eliminate efflorescences, followed by a soaking in a very hot dilute solution of Savlon, before being dried and varnished. Whether serendipitous or not, this seems to have been effective for some specimens, for example, marcasite in a chalk matrix, where subsequent decay was restricted to unvarnished areas. As with the palaeontological specimens, the result has seriously defaced the specimens, leaving an unnatural dark brown tarnished surface, especially noticeable with the chalcopyrite specimens from Cornwall.

The mineralogical catalogues record a substantial number of de-accessions and disposals because of pyrite decay at this time, reflecting the fact that if a mineral has decomposed, it has no chemical or morphological value to merit its retention. In certain cases the iron sulphide mineral formed the matrix to a species of greater significance, for example ludlamite or vivianite from Wheal Jane, Cornwall. In these cases the crystals of the more rare mineral were picked out and preserved and the iron sulphide matrix was discarded.

In the historic petrological collections, pyrite-bearing specimens with decay had mostly been discarded before any cataloguing had commenced. The research petrological collections from the Department of Earth Sciences are largely igneous and metamorphic in scope. However, upgrading storage boxes and updating catalogues has provided an opportunity not only to re-house the collections in better storage conditions, but also to easily identify which boxes, if any, hold the potential for pyrite decay.

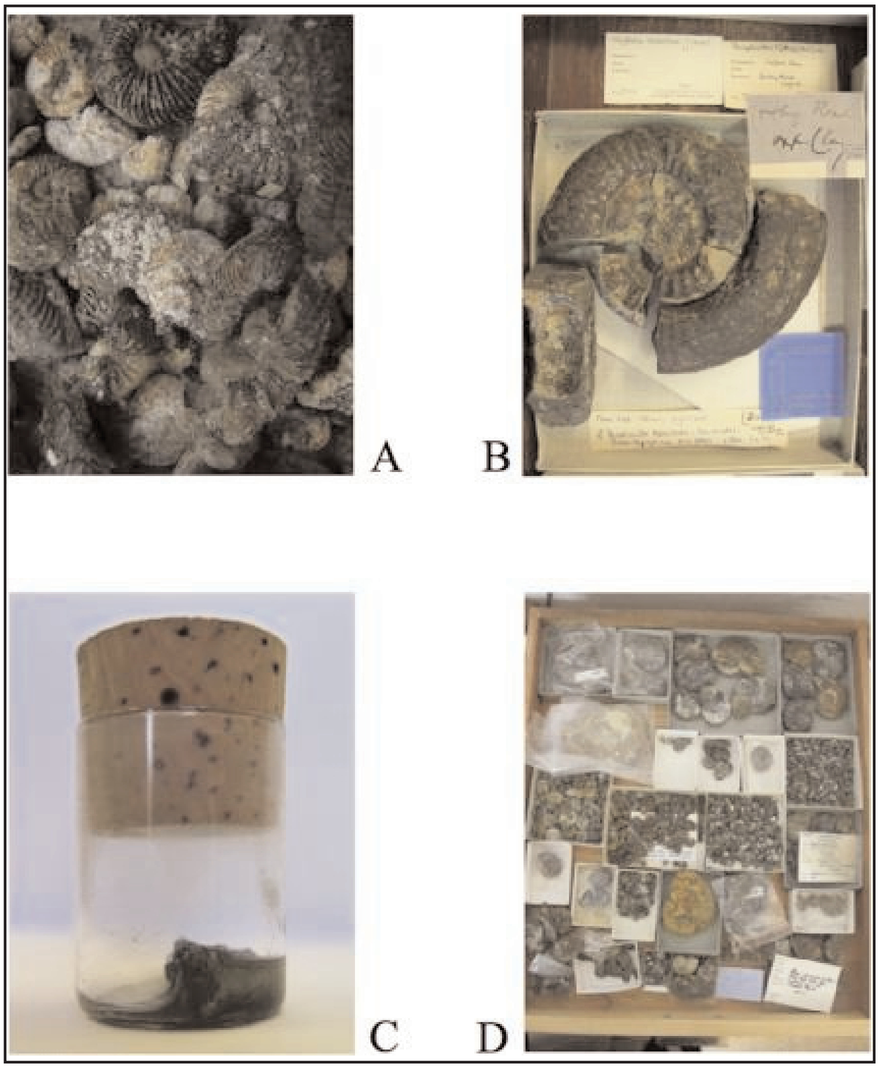


Figure 1: Examples of pyrite decay. A : White efflorescence of iron sulphate on some ammonites. B : Cracking due to expansion of decaying pyrite. C : Glass phial containing ammonite specimen that has produced visible liquid sulphuric acid. Specimens in this state may simply be discarded, but given the chemical hazard presented should be dealt with carefully using PPE. D : Drawer of uncatalogued ammonites affected by pyrite decay. In examples like this, severely decayed specimens are discarded and the remainder catalogued before being bagged.

1990s management of pyrite decay in the mineralogical collections

During the 1990s, work commenced to survey the mineralogical collections, neutralize oxidizing specimens using dry ammonia gas, and store them in lower humidity microclimates using plastic Stewart boxes and conditioned silica gel, in common with best practice in other museums at this time.

By then, the environmental conditions of the store, both inside and outside of the drawers, were being monitored using an Eltek telemetric system, as well as digital thermo-hygrometers. Humidity levels in the wider store-room varied within the range 29-73%. For at least 15% of the time during the period from early May until the beginning of October, when the central heating was off, humidity levels in the store-room would exceed the 55-60% range within which the percentage oxidation in framboidal / microcrystalline pyrite starts to rapidly increase. Indeed, for at least 85% of the time, the humidity levels would exceed the 35-40% range within which moisture absorption in such pyrite starts to become significant (Howie 1992b). However, monitoring also revealed the very effective buffering provided by the oak-drawer storage cupboards, which were keeping humidity levels steady within an annual range of 33-47%, crucially below that range within which percentage oxidation starts to rise significantly, even during those critical times of the year when the heating was off.

The whole collection was systematically surveyed for pyrite decay, with any potentially-oxidizing specimens noted using a 1 - 5 sliding scale of decay, similar to that described below for the current project [see Stage 1 : Surveying, below]. At this time, the mineralogical collections comprised less than 30,000 specimens, and those that were deemed to be suffering from various levels of pyrite decay numbered approximately 380, of which c. 250 were eventually treated with ammonia. Others, whose chemistry was not considered suitable for ammonia treatment, were stored with magnesium chloride ($MgCl_2$)-conditioned silica gel only.

Starting with the worst-case pyritic specimens, ammonia treatment to neutralize the acidic oxidation reactions was conducted in batches, using the method described by Waller (1987). Ammonia solution (35%) was mixed with the strongly hydrophilic polyethylene glycol PEG 400, in a volumetric ratio of 1 : 4.4, in order to lower the humidity in the treatment container. The specimens were left in this environment for a few days, until the colour change in an enclosed indicating tube of ferrous sulphate with glass beads showed that the reaction was complete. Excess ammonia was then allowed to dissipate from the specimens (off-gassing), by placing them in a desiccator with dry silica gel, changing this as necessary.

Prior to treatment of the specimens, a cost-effective mix of indicating and non-indicating silica gel was conditioned with a saturated solution of magnesium chloride salt (equilibrium RH 33%) within several desiccators, described in Irving (2001), to ensure that the resultant silica gel, when placed in Stewart boxes with the specimens, would buffer the micro-climate therein to approximately 33% RH for as long as possible. Magnesium chloride was selected because its equilibrium RH is a compromise between two competing outcomes which ideally require differing RH levels : the need to prevent the onset of rapid moisture absorption in pyrite, whilst at the same time avoiding dehydration changes in any associated minerals on the specimen.

The specimens were then placed in Stewart boxes of various sizes, with the appropriate quantity of conditioned silica gel per volume of box (Irving 2017a), adapted from Thomson's (1977) work with exhibition cases.

A conservation database for mineralogical specimens was set up using Microsoft Access, to include not only the accession details of each specimen, but also initial condition reports, associated photographs, treatment details, any changes engendered by the treatment, storage location within the collections, which specimens were treated and stored together within the batch, and a rolling annual maintenance programme of silica gel changing, with reports updated yearly. The database was later extended to include untreated specimens stored with silica gel in Stewart boxes and also those stored in oxygen-free micro-climates.

1990s management of pyrite decay and other vulnerable specimens in the palaeontological collections

The palaeontological collections were dealt with similarly to Mineralogical Collections at this time, except that only the invertebrate Jurassic (c. 70,000 specimens) and London Clay (Eocene) collections (c. 1,000 specimens) were systematically surveyed, due to a lack of staff time.

As with the mineralogical collections, a separate conservation database for palaeontological collections was set up, with a similar annual maintenance programme of silica gel changing and updated yearly reports. Again, the database was later extended to encompass untreated specimens stored with silica gel in Stewart boxes as well as those to be stored in oxygen-free micro-climates.

Storage in Stewart boxes for non-pyritic vulnerable specimens was on an *ad hoc* basis. For instance, a few specimens stored in the Museum Court, which were subjected to huge diurnal swings of humidity / temperature, were stored with silica gel conditioned with potassium carbonate. This was to buffer the micro-climate to c. 43% RH, in order to prevent drying out and / or delamination.

Nearly all specimens found with pyrite decay (c. 420 individual or groups of specimens), including those consisting of hydrous aluminium phyllosilicates, i.e., clay minerals, such as shale or mudstone, were stored with silica gel conditioned with magnesium chloride, after first being treated with ammonia. By buffering the micro-climate to c. 33% RH, it was hoped to prevent the onset of rapid moisture absorption conducive to further pyrite decay, whilst also avoiding dehydration changes in the clay matrices. However, this did not always go according to plan, with off-gassing, especially from those with a clay matrix, contributing to high humidity levels over the course of the year (Irving 2017b) and consequent recommencement of pyrite oxidation, thus occasioning the need for re-treatment in some cases.

Long-term studies to prolong storage times

During the early 2000s, long-term studies were undertaken to determine whether it would be possible to usefully extend the time between silica gel changes for all sizes of buffered Stewart box micro-climate. 'Usefully' in this context would mean a box 'surviving' for at least two years instead of one, thus reducing the workload. This involved sealing the lids of currently-in-use Stewart boxes with aluminium Scotch tape in order to reduce air changes, and comparing that year's temperature and humidity data, collected by TinyTag Ultra data loggers, with that from the same unsealed boxes, collected in a different year (Irving 2017b). It was hoped that this might be used as a relatively inexpensive interim solution until oxygen-free storage became a reality.

'Survival rates' were defined by the time taken for the RH in a Stewart box to exceed 33% [see '1990s management of pyrite decay in the mineral collections', above]. The results were interesting. Specimens contributed as much to the variability in survival rates as did the volume of the boxes / silica gel. Thus, boxes containing actively oxidizing specimens, many bearing hygroscopic oxidation products, or a porous matrix still off-gassing from the ammonia treatment, survived for less time than those boxes where specimens bore fewer oxidation products, were not off-gassing, and whose oxidation had been successfully neutralized. However, even taking this into consideration, **unsealed** used boxes containing

conditioned silica gel were extremely unlikely to survive a year at c. 33% RH. Even for **sealed** boxes, only those > 3.5 litres in volume were likely to survive for a year at c. 33% RH until the next silica gel change, which was somewhat concerning.

Boxes containing dry silica gel fared better, since the initial RH (15%) starts much lower and therefore takes longer to reach 33%. Even so, unsealed boxes are unlikely to survive longer than 1 year for any size of box, and for boxes of approximately 1 litre or below, survival will be much less than 1 year. However, despite the results being based on a very small, highly variable sample size, all sealed boxes of < 3.5 litres in volume should survive for two years, and those of 3.5 litres and above will survive for at least three years, using the appropriate quantity of dry silica gel.

The advantage of using dry silica gel in sealed Stewart boxes is that it is a much less expensive and quicker alternative to anoxic storage, particularly for specimens that require only temporary storage, as with new acquisitions prior to registration. If most specimens can tolerate the dry environment created in hours by the use of RP-A sachets [see 'Stage 2 : Anoxic storage process', below], then storage in an initial oven-dry micro-climate of 15% RH followed by a steady slow rise towards 33% RH over 2 or 3 years, will give plenty of time for environmental adjustment, whilst still keeping the % RH low enough to prevent the onset of pyrite decay. The disadvantage is that sealing with aluminium tape must be done very well to achieve the best results, and such high standards can be difficult to maintain.

The Current Project - Part 1

A problem with the existing storage in Stewart boxes has been the unsustainable, labour-intensive nature of changing the silica gel annually, as well as the difficulty of ensuring that the humidity levels in the boxes remained low enough to prevent re-oxidation. In addition, decreasing staffing levels has meant that a large number of mostly palaeontological specimens were not included in the programme, and to deal with these in the same way would have created an even larger annual workload. A new solution was needed.

First forays into anoxic storage

The planning of the current project commenced after the NOOX3 conference at the Natural History Museum, London (NHM), in 2003, and a detailed report on what was discussed there and recommendations on how to proceed was written (Irving 2003). However, because of the high cost of equipment, the project was put on hold until finance could be made available. In the meantime, the opportunity was taken to update the Minerals database with detailed species identification for those specimens which were awaiting anoxic storage, as only minimal information had been recorded when these specimens were first accessioned over a century previously. It was around this time that the serendipitous effects of the earlier Savlon 'treatment' were noted [see Past treatment of 'pyrite decay' in the Museum, above]. For some specimens, what initially appeared to be the oxidation products of pyrite decay were found to be the Savlon coating breaking down. Since this coating had provided a protective barrier for 40 years, when it would appear that so many specimens had been previously lost to this 'treatment', it is probable that the survivors were those with very little oxidation to start with, or indeed, none at all.

Pilot project

Planning for the pilot project established the basic criteria and procedures on which the project would later build. From the outset, with finances tight, but wanting the longest possible storage time for the specimens, the decision was made to create double anoxic storage bags, each from two types of barrier film, the transparent, but very expensive Escal, and the opaque, but much-less-expensive aluminium laminate, Marvelseal 360. Bags made entirely from Escal (a 7-layered oriented polypropylene /silica-deposited polyvinyl alcohol / low density polyethylene laminate) would only be used in exceptional circumstances, for instance, for high priority large specimens, where the normal 2-dimensional bag shape [see Figure 3] would not be practical.

Escal and Marvelseal were chosen because both barrier films at the time of planning had similarly desirable low gas migration rates (oxygen : 0.05 cc / m^2 / 24 hrs; water vapour : 0.01 g / m^2 / 24 hrs; @25°C; 60% RH) (Murabayashi 2012). Escal has now been replaced by Escal Neo, which has higher water vapour and oxygen migration rates (Waller 2018), further justifying the decision to create double anoxic storage bags. However, it is still the best transparent barrier film for longer-term museum needs.

Since seals are always the weakest point, welding together two different types of laminated barrier film would require some experimentation with a heat sealer to determine (a) whether a 6mm or 9mm seal width would produce the least amount of wrinkling with two different laminates, and (b) which combination of weld and cool settings, in each case, would produce the strongest seals. Wrinkling tends to weaken the seals, allowing an increase in gas exchange, with a consequent reduction in bag longevity.

A couple of heat sealer manufacturers / retailers (Hulme-Martin, etc. 2009) were enlisted to weld together samples of the OUMNH's two laminates using the same make(s) / model(s) of impulse heat sealers under different specified criteria as mentioned, with the promise of a purchase for the most successful set of outcomes. The results of the returned samples showed that a 6mm seal width produced the least amount of wrinkling using an HMS Star-91 impulse heat sealer; and from the range of different weld / cool settings, it could be determined which was the optimum combination for seal strength, by gently trying to pull the two laminates apart. The strongest seal appeared to be 4 seconds on the weld setting, followed by 7 seconds on cool, though this has since been further refined to be slightly longer in each case. For added strength and longevity, it was decided to produce triple seals with a 0.5cm gap between each seal, since the gaps / extra seals also help to mitigate the effects of wrinkling.

A spreadsheet was then set up to calculate the size and volume of bags required for each specimen, or group of specimens, with extra allowances made for seal widths and any later opening [see Table 2 and 3. Calculation of bag sizes and allowances for re-sealing, below]. From the calculated air capacity, the exact number of RP oxygen-absorbing sachets required per bag could easily be determined. This made the best use of materials, so that there was very little waste.

The pilot project was eventually completed in 2011, according to the above criteria and procedures. A batch of mineralogical specimens of similar height were chosen, as these would require a similar surplus when making allowances for a crease-free final seal [see 3. Calculation of bag sizes and allowances for re-sealing, below]. So far, the pilot project is judged to have been successful, since none of the indicators (humidity strips and bags of indicating silica gel) show any visible signs of change after 7 years.

Time trial and feasibility study

With the setting up of a planning team in 2013, comprising all of the Earth Collections staff, the project received further impetus. Initially, a priority checklist of pyritic formations and localities was produced. However, it was soon realized that a systematic on-site palaeontological survey was required to determine the extent of pyrite decay in the collections. At the same time, a time trial was conducted to find out how long it would take to bag each batch of specimens (Irving 2013). A batch in this context is the number of specimens required to use up all of the 25 RP-A oxygen-scavenging sachets supplied in one vacuum-sealed bag. The time trial included locating and organizing specimens, as well as the weighing, measuring, recording and data entry for the spreadsheet calculations, which determined the bag size for each specimen (or collective), and every aspect of bag-making according to predetermined criteria. The results indicated that c. 75 person-hours were required to place 25 specimens into double bag anoxic storage. The process of making bags for anoxic storage is discussed in detail in Part 2. In the light of the results, the suggestion was made that the use of templates for cutting the barrier films would make the process more efficient, especially when different volunteers may be involved.

A feasibility study into adopting a few standard bag sizes was also undertaken. This exercise showed that this would save neither time nor money. Standard bags would take just as long to cut and lay out as more-tailored bags; would waste more in the way of expensive film and oxygen absorbing sachets, due to the extra width and length of each bag required to accommodate the less-tailored sizing; and using fewer standard bag sizes would increase the number of larger bags, which would take twice as long to seal, as the long side would be longer than the width of the sealing machine. Numbers and sizes of standard bags would also need to be worked out for every batch, otherwise time could be wasted measuring and cutting particular sizes of bags that were ultimately redundant, whilst having to make time to include more of another size. As an example, for the particular batch of 25 specimens chosen, in order to accommodate the less-tailored sizing, calculations showed that just to keep within a workable 5cm extra in the width and length of each bag, it would still be necessary to cut 4 inner and 3 outer bag sizes. The fewer the sizes of bag, the more expensive the whole process becomes, whilst not actually saving any time.

Intern project

An 8-week intern project was then set up in the palaeontological collections (Fish 2014). The first part of this was to systematically survey as much of the on-site collections as possible to determine the extent of pyrite decay, whilst at the same time assigning a number to any oxidizing specimens (or collective numbers of specimens) according to a sliding scale of decay [Stage 1 : Surveying, below]. The second part involved another time trial, this time incorporating the use of templates for cutting the barrier film bags. Whilst the final seal and associated preparations were excluded due to lack of time, comparisons with tasks in the previous time trial suggest that where only one person is involved, the use of templates saves very little time, if any. There are certain tasks, such as the sealing together of two pieces of barrier film to make each bag, which can only be done by one person. However, the use of templates does increase options for reducing project duration through parallel working by a couple of volunteers, as the cutting of templates, and marking and cutting of barrier films, does not need to be a one-person task.

Thus, in the first time trial, approximately 37.5 person-hours were spent in measuring and cutting film for 50 bags (25 specimens). In the second trial, more-or-less the same time was spent in reaching the same stage. However, the second trial also included measuring and cutting bag templates, and laying out the templates on each film in turn [see Figure 2, below], before marking and cutting the film. The reason for the laying out of templates separately was to enable the best use of space on films of different width. If two people were to be involved, the length of time devoted to these particular tasks would be approximately 18.75 hours per 25-specimen batch instead of 37.5 hours. Thus the overall duration of placing one batch of 25 specimens into anoxic storage could be reduced from c. 2 weeks to c. 1.5 weeks.

The current project - Part 2

The current project has been largely focused on the palaeontological collections, though some of the mineralogical collections have also been included. Although past ammonia treatment and Stewart box microclimate storage is currently keeping specimens in the mineral collections in good condition due to voluntary annual maintenance by an ex-member of staff, this is not the case with the palaeontology collections. Since there are a large number of palaeontological specimens that have not been ammonia-treated or stored in suitable micro-climates, oxygen-free storage for such pyritic material has become a priority. A systematic survey of the entire on-site palaeontology collections was undertaken, followed by prioritization planning, to ensure that important specimens were placed into anoxic storage first.

It is important to note that volunteers have played an important role in the progress of this project, carrying out work at all stages of the anoxic bag-making process. These were recruited through the Oxford University Museums Volunteer Service, by putting together a role description and sending it out to everyone on the volunteer mailing list who had expressed an interest in collections work [included as Appendix I]. Without volunteers, the project may not have have progressed from planning to reality, and we are very grateful to them for their input.

Stage 1 : Surveying

With the employment of one of the authors (P.H.) as a temporary replacement for one of the Earth Collection staff on maternity leave, the systematic survey of the on-site palaeontological collections (c. 400,000 specimens) for specimens with pyrite decay was completed. Each was photographed, measured, and the level of decay recorded on a scale of 1 - 5, according to the following criteria (Fish 2014) :

1. Surface discolouration, minimal cracking or slightly powdery / friable sediment (or strong pyrite decay smell - suggests internal decay).

2. Powdery / friable areas on fossil surface or slight

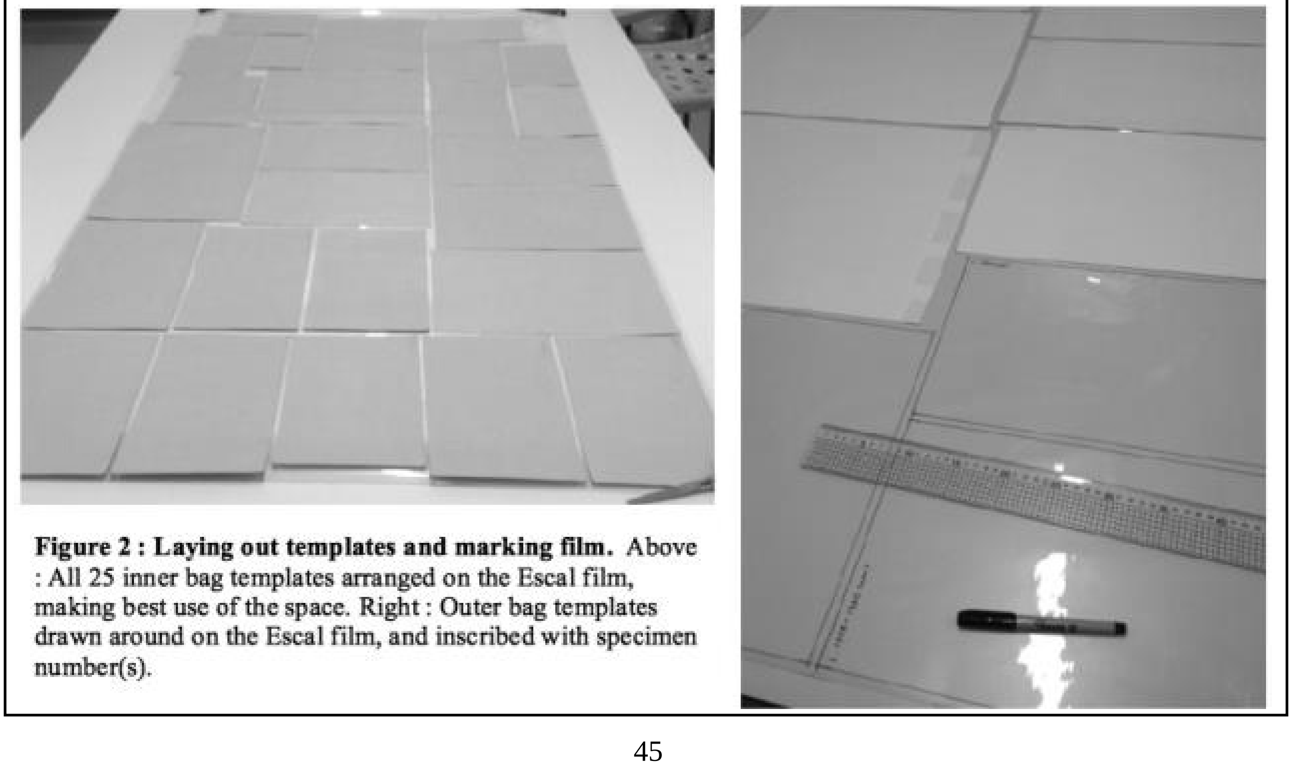


Figure 2 : Laying out templates and marking film. Above : All 25 inner bag templates arranged on the Escal film, making best use of the space. Right : Outer bag templates drawn around on the Escal film, and inscribed with specimen number(s).

cracking from expansion of internal pyrite/sediment.

3. Larger areas of powdery / friable material, severe cracking from expansion or evidence of pyrite decay beneath fossil surface.

4. Fossil mostly covered with powdery / friable material, highly fragile, fossil broken apart by expansion or evidence of pyrite decay throughout specimen.

5. Fossil entirely / nearly completely decayed, no longer holding shape, falls apart when moved.

This rating system is a rough guide only, and can be subjective. Ratings may also differ with the amount of pyrite decay relative to the size of the fossil. The data was then recorded on the Decay Survey spreadsheet [see Table 1].

The survey identified 1256 individual or groups of specimens with pyrite decay, predominantly from the Mesozoic and Cenozoic Eras with much smaller numbers from the Palaeozoic.

Stage 2 : Anoxic storage process

Developing an overall strategy was important for planning the vast amounts of work ahead to ensure that the project was efficient, correct materials were used and appropriate solutions found for different types of problem. These tended to evolve as problems became apparent.

1. Prioritization

Current problems

In order to deal with the significant numbers of palaeontological specimens identified with pyrite decay issues it was decided to prioritize them in order of importance. The Decay Survey spreadsheet was used to rank specimens in a priority order [see Table 1]. Those to be dealt with first (Priority 1) included type and figured specimens, those from rare localities, material with very good data (e.g. ammonites from a known horizon), or material with high research potential. All other accessioned material was Priority 2. At the bottom of the priority list (Priority 3) were unaccessioned specimens lacking data, and where no taxonomic information could be gleaned because of heavy pyrite oxidation. The latter are likely to be disposed of in accordance with SPECTRUM guidelines.

Future prevention

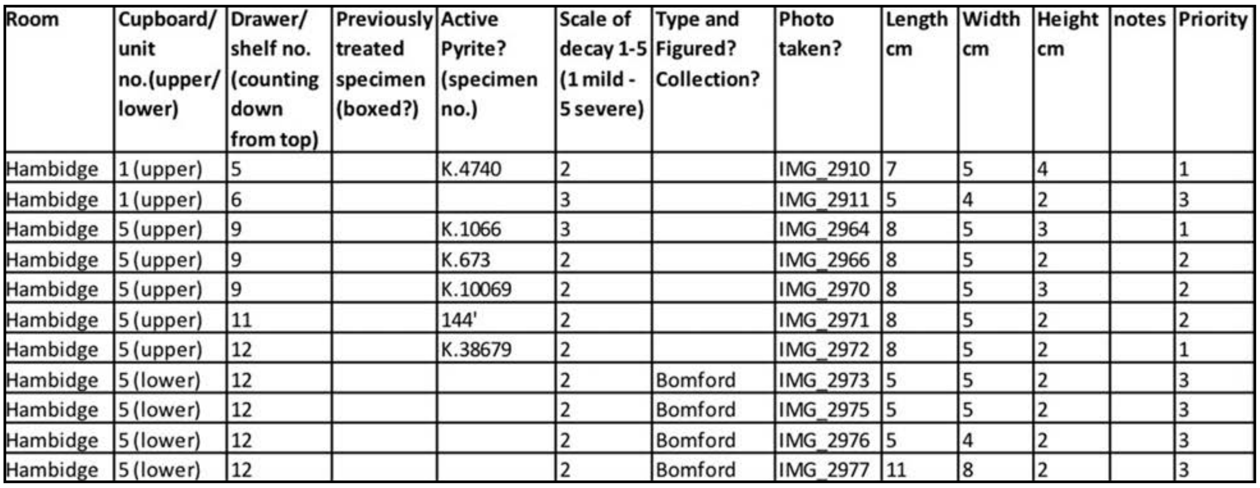
Some pristine mineralogical specimens have been placed into anoxic storage as a preventive measure to stop them decaying. The same will be done with other newly-aquired pyritic material [see also 'Long-term studies to prolong storage times', above].

2. Choice of materials

Materials were chosen based on discussions, research presented, and other museums' experiences at the NOOX3 conference at the NHM in 2003 (Irving 2003).

A combination of barrier films was chosen to create the bags for anoxic storage, in order to keep costs down whilst still retaining the necessary transparency [see 'Pilot project', above]. The opaque barrier film Marvelseal 360 is used for the bottom layer of the bag, and on the top is the clear barrier film Escal. The size of each bag is calculated to allow space for the oxygen scavenger, humidity indicators and, if necessary, extra space for opening and re-sealing later.

The oxygen scavenger, RP-A, which absorbs all gases, including water vapour, is used as a default where a dry internal bag atmosphere is not a problem, whereas RP-K, which will absorb all gases except water vapour, is used for material with a clay-based / shale matrix, so as to prevent drying out of the specimens. Conservation grade materials, such as tape for securing card trays to the inner bag, are used throughout.



Room	Cupboard/ unit no.(upper/ lower)	Drawer/ shelf no. (counting down from top)	Previously treated specimen (boxed?)	Active Pyrite? (specimen no.)	Scale of decay 1-5 (1 mild - 5 severe)	Type and Figured? Collection?	Photo taken?	Length cm	Width cm	Height cm	notes	Priority
Hambidge	1 (upper)	5		K.4740	2		IMG_2910	7	5	4		1
Hambidge	1 (upper)	6			3		IMG_2911	5	4	2		3
Hambidge	5 (upper)	9		K.1066	3		IMG_2964	8	5	3		1
Hambidge	5 (upper)	9		K.673	2		IMG_2966	8	5	2		2
Hambidge	5 (upper)	9		K.10069	2		IMG_2970	8	5	3		2
Hambidge	5 (upper)	11		144'	2		IMG_2971	8	5	2		2
Hambidge	5 (upper)	12		K.38679	2		IMG_2972	8	5	2		1
Hambidge	5 (lower)	12			2	Bomford	IMG_2973	5	5	2		3
Hambidge	5 (lower)	12			2	Bomford	IMG_2975	5	5	2		3
Hambidge	5 (lower)	12			2	Bomford	IMG_2976	5	4	2		3
Hambidge	5 (lower)	12			2	Bomford	IMG_2977	11	8	2		3

Table 1 : Decay Survey spreadsheet.

Humidity indicator cards are preferentially used in place of oxygen 'eyes', as these are more reliable indicators over the longer term for internal gas absorption by the RP-A oxygen scavengers. However, when using RP-K, oxygen 'eyes' are included in the inner bags with the humidity indicator card, since otherwise there is no reliable way of knowing whether the inner bag has been correctly sealed.

Where the use of oxygen scavengers is uneconomic, e.g., when temporarily bagging newly-acquired specimens prior to registration, or when larger bags need to be made to accommodate awkward-shaped or larger specimens, then a specific quantity of dry or conditioned silica gel is used instead of the RP sachets. The type of material will dictate whether to use dry silica gel, or that conditioned by magnesium chloride (33% RH) or potassium carbonate (43% RH) (see notes for Table 3 for the rules determining this choice). Calculations of quantities to be used, adapted from Thomson (1977), are based on the air capacity of the inner bag, and though they directly correlate with the quantities calculated previously for Stewart box storage, bag survival times undoubtedly will be longer because air exchange via the barrier films and triple-seals is much reduced compared with Stewart boxes.

Higher priority palaeontological specimens and all minerals are double-bagged in order to maintain a stable micro-climate for these specimens for as long as possible. The outer bag provides an extra protective barrier in case of careless handling or damage by sharp objects, and by effectively providing double the gas barrier, also increases the long-term stability of the micro-climate in the inner bag. Low priority and temporarily-bagged specimens may only be single-bagged, because of time and / or cost restraints.

Including a small pierced bag of dry indicating silica gel within the outer bag will show at a glance whether the outer bag has become damaged at some future time. Similarly, an RH strip in the inner bag will show whether the specimen has pierced the inner-bag material, as any differences between the humidity levels in the inner and outer bags will then equilibrate. Specimen labels are also normally placed in the outer bag as protection against damage or loss, which could occur if the labels are attached to the outside of the bag. A self-seal bag is used to corral the specimen labels, which can then be taped into place to prevent the labels being obscured by the inner bag and its contents [see Figure 3].

Placing a 3-dimensional object into a 2-dimensional bag can be a challenge, with some oddly-shaped specimens and those with sharp projections proving more of a challenge than others. These are placed in the bags in deep card trays with Plastazote padding to stop them damaging the bag. Any extra height so produced needs to be taken into consideration when measuring dimensions for bag calculations [see Table 3. Calculation of bag sizes and allowances for re-sealing, below].

Glass tubes are placed on their sides in a tray, leaving the specimens visible, while the lids are replaced with loose Plastazote bungs, pre-cut in-house, to allow for gas exchange.

As far as is practical, multiple specimens of the same species from the same locality are placed in the same bag, in order to save time and material usage. Specimens that share the same card tray are separated by Plastazote, where practicable, in order to prevent abrasion.

3. Calculation of bag sizes and allowances for re-sealing

Bag size and air capacity are calculated using a spreadsheet [see Table 2]. These are determined using the maximum dimensions (length, width, height), weight and specific gravity of the object to be enclosed. Knowing the air capacity of the inner bag, it can be determined how many RP sachets will be required depending on whichever size of sachet is to be used. For instance, when using RP-A-5 sachets (absorption up to 500ml), a 900ml volume will require two sachets, and 1600ml will require four. The spreadsheet will also calculate an allowance for extra bag-size and air capacity (shaded columns), to be used if later opening and re-sealing is known to be required, i.e., if it is highly likely that researchers will need later access, or for temporarily-bagged material. The spreadsheet is based on a method for working out the required bag size downloaded from the website of Conservation-by-Design (2009a), now known as CXD. The pdf is available from the company on request, but an updated version is in their current catalogue.

The column titles of the spreadsheet are reasonably self-explanatory, though it may be helpful to know that 'Standard Capacity' refers to bag sizes calculated **without** any extra allowed for later specimen removal. 'Standard Capacity' is also to be referred to after 'Extra Capacity' bags have been later opened, in order to check whether there will need to be any change in the quantity of RP sachets to be included before the bag is re-sealed, since there will be reduced air capacity in such bags.

The seal allowance numbers in the first three rows probably need some clarification: As the bags are triple-sealed, then the total width includes an extra 8cm (2 x 4cm) for the two long side seals.

Similarly, the total length calculation allows for an extra 8cm for the two shorter top and bottom seals, but also includes an extra 8 cm to allow for a crease-free final seal, necessary because of the difficulty of sealing in a 3-dimensional object into a 2-dimensional bag. It is important to leave a surplus in the total length equivalent to the height, and in this case, it was decided to allow 8 cm, since none of the specimens (or their card trays) were above this height. This number can be varied depending on the height of the batch of specimens chosen.

The 6cm allowance for later re-sealing, refers to the columns in green, and takes into account the extra required to allow for a reduction in length which would occur if the bag is later opened.

Specific gravity (S.G.) is the ratio of a material's density with that of water at 4°C (where it is most dense and is taken to have the value 999.974 kg. m-3) and is therefore a relative quantity with no units. The minerals that most commonly make up the outer surface of the Earth's crust have an average specific gravity of 2.75, while pyrite has an S.G of approximately 5. Therefore for palaeontological material, an S.G. of 2.75 is assumed for the matrix, and then depending on the proportion of pyrite present, a 'rough and ready' S.G. is worked out for each specimen. The proportion of dense pyrite to less-dense matrix will have an effect on the air capacity of the bag, which could affect the number of RP sachets required.

4. Check-list for staff and volunteers

Since it is necessary to be very systematic in gathering together the various items to be placed in either the inner or outer bag, an easy-to-follow guide, including a set of tables for different priorities and types of material, has been printed and placed in the lab as a check-list for use by staff and volunteers. As an example, the check-list for high priority specimens is included here as Table 3, below.

5. Final Sealing

Organization is key to minimizing the amount of time that RP oxygen-absorbing sachets are exposed to the air, once removed from their vacuum-sealed bag. So, for each batch to be bagged, a production line was set up, with up to 3 volunteers assigned specific duties in the final sealing process. Items to be sealed in with the specimen(s) in the inner bag, except for the RP sachet(s), were gathered together in advance and checked against the above table [see Table 3].

Conservation-grade tape was used to secure items in place, as necessary, within the inner and outer bags before the final sealing. This avoids enclosed items becoming obscured by movement of other bagged items during later handling, which can be especially problematic when sealing one bag inside another.

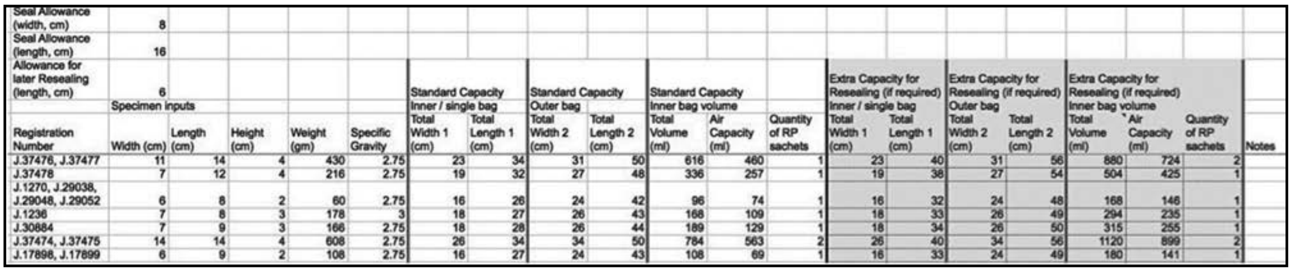
Once the sealed bag containing the RP sachets was opened, sachets were handed out quickly according to requirements, enough for one inner bag at a time. That inner bag was then immediately triple-sealed. A heavy-duty plastic clip was used between-times to temporarily re-seal the bag containing the remaining RP sachets.

Similarly, items to be enclosed in the outer bag, together with the now-sealed inner bag, were gathered together, checked, and secured in position before the final seal. Each bag was again triple-sealed, as a precaution against excessive wrinkling caused by the use of two different barrier films. After final sealing, the date of bagging was written on the finished bags [see Figure 3].

All actions taken, including final storage location, were recorded on a spreadsheet, and the database records for the specimens were also updated with this information.

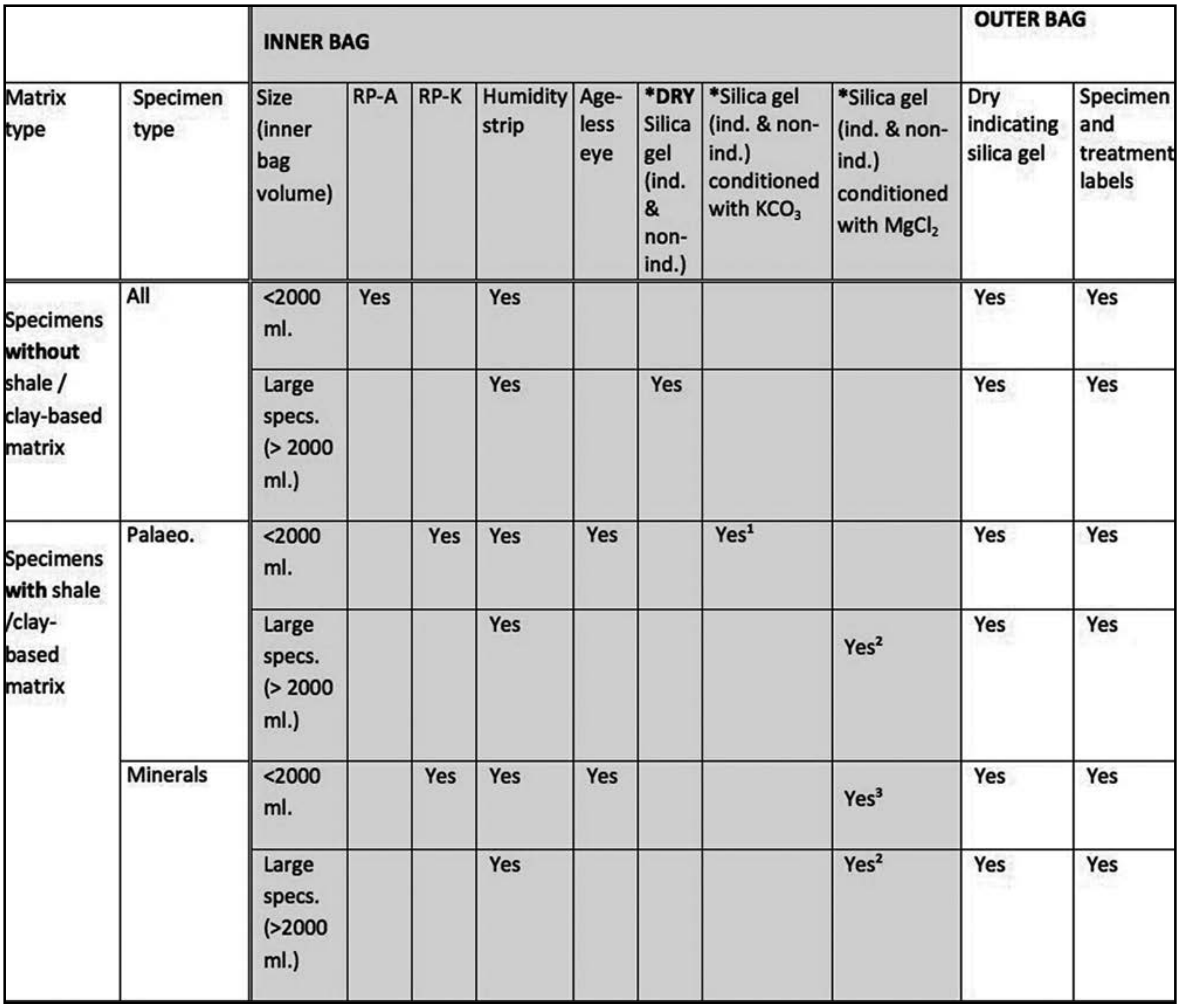
Stage 3 : Monitoring and maintenance

The specimens bagged are to be monitored on an annual basis. It is hoped the double bags will last for at least 15-20 years, and single bags for up to 8-10 years. This is a best guesstimate based on a pdf



Seal Allowance (width, cm)	8																			
Seal Allowance (length, cm)	16																			
Allowance for later Resealing (length, cm)	6					Standard Capacity		Standard Capacity		Standard Capacity			Extra Capacity for Resealing (if required)		Extra Capacity for Resealing (if required)		Extra Capacity for Resealing (if required)			
	Specimen inputs					Inner / single bag		Outer bag		Inner bag volume			Inner / single bag		Outer bag		Inner bag volume			
Registration Number	Width (cm)	Length (cm)	Height (cm)	Weight (gm)	Specific Gravity	Total Width 1 (cm)	Total Length 1 (cm)	Total Width 2 (cm)	Total Length 2 (cm)	Total Volume (ml)	Air Capacity (ml)	Quantity of RP sachets	Total Width 1 (cm)	Total Length 1 (cm)	Total Width 2 (cm)	Total Length 2 (cm)	Total Volume (ml)	Air Capacity (ml)	Quantity of RP sachets	Notes
J.37476, J.37477	11	14	4	430	2.75	23	34	31	50	616	460	1	23	40	31	56	880	724	2	
J.37478	7	12	4	216	2.75	19	32	27	48	336	257	1	19	38	27	54	504	425	1	
J.1270, J.29038, J.29048, J.29052	6	8	2	60	2.75	16	26	24	42	96	74	1	16	32	24	48	168	146	1	
J.1236	7	8	3	178	3	18	27	26	43	168	109	1	18	33	26	49	294	235	1	
J.30884	7	9	3	166	2.75	18	28	26	44	189	129	1	18	34	26	50	315	255	1	
J.37474, J.37475	14	14	4	608	2.75	26	34	34	50	784	563	2	26	40	34	56	1120	899	2	
J.17898, J.17899	6	9	2	108	2.75	16	27	24	43	108	69	1	16	33	24	49	180	141	1	

Table 2 : Spreadsheet used to calculate bag size, air capacity and RP oxygen scavenger requirements.



		INNER BAG								**OUTER BAG**	
Matrix type	**Specimen type**	**Size (inner bag volume)**	**RP-A**	**RP-K**	**Humidity strip**	**Age-less eye**	***DRY Silica gel (ind. & non-ind.)**	***Silica gel (ind. & non-ind.) conditioned with KCO_3**	***Silica gel (ind. & non-ind.) conditioned with $MgCl_2$**	**Dry indicating silica gel**	**Specimen and treatment labels**
Specimens without shale / clay-based matrix	**All**	**<2000 ml.**	**Yes**		**Yes**					**Yes**	**Yes**
		Large specs. (> 2000 ml.)			**Yes**		**Yes**			**Yes**	**Yes**
Specimens with shale /clay-based matrix	**Palaeo.**	**<2000 ml.**		**Yes**	**Yes**	**Yes**		**Yes[1]**		**Yes**	**Yes**
		Large specs. (> 2000 ml.)			**Yes**				**Yes[2]**	**Yes**	**Yes**
	Minerals	**<2000 ml.**		**Yes**	**Yes**	**Yes**			**Yes[3]**	**Yes**	**Yes**
		Large specs. (>2000 ml.)			**Yes**				**Yes[2]**	**Yes**	**Yes**

1 To ensure consistency, no matter what the ambient RH is when bagging, palaeo. specimens (< 2000ml) in clay should be stored with silica gel conditioned with KCO_3 (43% RH) as well as RP-K. This is because the matrix and the specimen will mostly consist of the same clay-based material.

2 Unfortunately, for both large palaeo. and mineral specimens (> 2000ml), RP-K becomes rather uneconomic, so in the absence of large RP-K sachets, then specimens should be stored with silica gel conditioned with $MgCl_2$ (33% RH) only. This is a compromise between there being too much desiccation (dry silica gel) for clay matrices, and the increased risk of re-commencement of pyrite decay by using silica gel conditioned with KCO_3 (43% RH) without RP-K, in an inner bag containing oxygen.

3 To ensure consistency, no matter what the ambient RH is when bagging, mineral specimens (< 2000ml) in clay should be stored with silica gel conditioned with $MgCl_2$ (33% RH), as well as RP-K. This lower % RH is a compromise to reduce risk, since mineral specimens may contain many different species (including pyrite) on one specimen, each with different sensitivities to pyrite decay, with only the matrix being clay-based.

Table 3. Check-list for HIGH PRIORITY (P1) specimens to be DOUBLE-BAGGED - Anoxic Storage / Silica Gel.

downloaded from the website of Conservation-by-Design (CXD 2009b), which suggests that single bags with a single seal should survive 6 - 8 years. It is hoped that by triple-sealing the bags, storage times will be prolonged further.

If any are later opened for research, this will need to be done with care and under supervision, so that only the seal is removed, and damage to the barrier film(s) is avoided. The now smaller bags will need to be later resealed enclosing new oxygen scavenger RP sachets. The spreadsheet shown in Table 2 includes columns which show the calculation for the new smaller standard bag capacity, to enable adjustments in the number of RP sachets if necessary. This is designed as a cost-saving exercise, since using too many RP sachets is expensive.

Figure 3 : A finished bag using RP-A sachets.

Problems still to be addressed / future plans

Large specimens that are too big to be placed in anoxic bags, such as whole mounted marine reptiles with decaying stomach contents, need to be dealt with by other means. There are plans to improve the environmental conditions of such large fossils in the Vertebrate Compactor Room (VCR) by the installation of some form of plant for environmental control, though discussions are still ongoing over the practicalities and funding for the project.

The majority of minerals requiring anoxic storage are currently stored in Stewart boxes with conditioned silica gel, which is changed annually. This will become unsustainable in the medium-term, relying as it does on an ex staff member. Thus, anoxic storage has now become a priority for these specimens. This has become even more urgent in the light of the results of the above-discussed long-term studies (Irving 2017b), which have shown that 'survival rates' (at c. 33% RH), for all Stewart boxes in the current annual maintenance programme, are actually much less than one year.

Results

Out of 400,000 palaeontological specimens surveyed, 1,256 individual records, equating to c. 2,000 specimens, have been found with various levels of pyrite decay. Of these, 281 records are for Priority 1 material. With the exception of fossils in the VCR, almost all the Priority 1 material has now been stored in anoxic micro-climates. This constitutes c. 165 double bags containing c. 300 specimens. In addition, approximately 40 individual mineralogical specimens were similarly dealt with. Thus, over the course of a year, with one member of staff (P.H.) spending 50% of his time on the project (c. 770 hours), and 8 volunteers working a total of 405 hours, 1,175 person-hours have been spent placing c. 340 specimens into 205 anoxic double-bagged micro-environments.

Assuming 1,175 person-hours equates to c. 10 batches of between 20 and 25 double bags per batch, depending on number of RP sachets required per micro-climate, then each batch required 117.5 person-hours to complete. This is half as much again compared with the time trials, which took c. 75 person-hours to complete [see Time trial and feasibility study]. However, the disparity here can be account-ed for by the amount of staff time spent initially in surveying, prioritizing and associated record-keeping, which will not need to be repeated. Therefore the actual person-hours required for bag-making and associated activities in the future should be closer to that in the time trials, and this will be used in the following estimations.

In the palaeontological collections, excluding all material in the VCR, for which environmental control is planned, there are 746 individual records of specimens still requiring anoxic storage. Of these, only 33% are considered to be Priority 1 (P1) and Priority 2 (P2) material, which is roughly the equivalent of 12 batches of double bags. Thus, at least 900 person-hours will be required to place P1 and P2 into anoxic double-bag storage.

In the unlikely scenario that anoxic storage could be justified for all Priority 3 (P3) material, then between c. 1,050 and c. 1,875 person-hours would be required for c. 25 batches of approximately 500 specimens, depending on whether single or double, or a combination of bags is to be used. However, as previously mentioned, it is likely that many specimens will be disposed of, although some may be placed into anoxic single-bag storage. It should be noted that, for each batch of c. 25 specimens, the number of person-hours is not halved by the use of single bags, as there are certain tasks which require the same amount of time, such as finding, organizing, weighing, measuring, recording, and data entry for bag-size calculations.

In the mineralogical collections, there are c. 400 specimens requiring anoxic storage, roughly equivalent to 19 batches, of which c. 250 are currently stored in Stewart boxes with silica gel. Since double bags will be used for all specimens, then c. 1,425 person-hours will be required to place all 400 specimens into anoxic storage, which is the equivalent of 1 person devoting 100% of his / her time to this project for about 1 year.

Thus, for Earth Collections as a whole, in the unlikely event that anoxic storage for all Priority 3 specimens could be justified, between 3,375 and 4,200 person-hours, or approximately 3 - 3.5 years, would be needed to complete the project with similar staffing levels and volunteer input. If all P3 specimens were to be excluded, then the project could be completed in 2,325 person-hours, or c. 2 years. The reality will lie somewhere between. With current staff workloads, even the latter may be quite difficult to achieve, but the hope is to continue the momentum with one or more conservation internships in the first instance.

Conclusions and recommendations

The project has shown that with forward planning and teamwork, organizing the project into manageable sections, establishing basic criteria and procedures, trialling such procedures, and making use of volunteer input, it has been possible to reduce costs, avoid wastage and save time. Knowing the scale of pyrite decay in the geological collections has enabled the project to prioritize specimens and to plan for its continuation into the future. As more vulnerable specimens are placed in anoxic / low humidity microclimates, the burden on staff is reduced, and the specimens' long-term preservation for future use is assured.

However, the planning and execution of the project has highlighted a few recommendations that, if followed, will definitely make the whole process run more smoothly.

- Set aside at least one large clean space dedicated to the process.
- Set aside specific days for specific work.
- Plan for where the finished bags are to be stored.
- Create spreadsheets for accurate recording of work and calculation of requirements.
- Conduct a pilot project to enable any procedural and / or calculation problems to be ironed out.
- Conduct a time trial to determine how long it will take to bag a batch of specimens from initial data entry to final sealing, so as to enable scaling up for the whole project.
- Make templates for all the bags in a batch and arrange them in such a way as to make the most efficient use of the barrier films.
- Using the templates, cut both of the barrier films simultaneously, if saving time becomes more of a priority than wastage of material (see below).
- Remember to label the template and each cut piece of barrier film with the corresponding specimen number, and whether it is to be used for the inner or outer bag.
- Produce a check-list in the work area for staff and volunteers to follow when gathering together the various items to be placed in either the inner or outer bag prior to final sealing.
- Purchase replacement ribbons and tape for sealing equipment in advance.
- Ensure that it is someone's responsibility to do the annual check once the specimens are bagged and stored, otherwise this will be forgotten.

The project has also thrown up one or two questions that have yet to be properly resolved :

Firstly, is it economically justified to use extra materials (including RP sachets) in producing many double bags with extra capacity in case of later opening for research, when this is likely to happen in relatively few cases? In such cases, time would only need to be spent making a new outer bag, since the old cut-down outer bag could be re-used as the new inner bag.

Secondly, in a project where cost-efficiency is a priority, how should the wastage of material be balanced against the cost of someone's time? For instance, time can be saved during the bag-cutting process by using templates to cut both barrier films at the same time. However, since Marvelseal 360 is wider than Escal Neo, then, if laying out templates to be cut simultaneously, then an extra 21 cm for the whole roll will always be wasted. Laying the templates separately on each roll will make the best use of materials, but will always take longer. If saving paid employees' time is a priority, then wasting one-sixth of the cost of a roll of barrier film, could probably be justified. However, with the use of volunteers' time, the balance would tip in the opposite direction.

The authors hope that the experiences of the OUMNH will be helpful to other institutions when planning and implementing their own anoxic storage project with limited time and resources.

Acknowledgements

The Authors wish to thank Juliet Hay, Eliza Howlett, Monica Price, Hilary Ketchum, Vicky Fish, Bob Irving, Paul Jeffery, André Ashington, numerous volunteers recruited through the Oxford University Museums Volunteer Service, Caroline Buttler at the National Museum of Wales, and Chris Collins at the NHM, London, for their invaluable work and advice during the planning and implementation of the project.

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Appendix I - Recruitment letter to volunteers

Volunteers needed to help package fossils and minerals for anoxic storage

About the Role

My name is Phil Hadland; I am currently doing maternity cover at the museum. I have been working on collections of fossils that contain pyrite, or fool's gold. Some of these suffer from pyrite disease. This is the degradation of pyrite when it reacts with oxygen and moisture in the air. It is a chemical reaction which produces small amounts of sulphuric acid and other reaction products. This can be very damaging to fossils, whether the pyrite is in the fossil itself or the surrounding sediment. Once we have established which specimens are affected we begin to treat them, transferring them to anoxic storage in order to stabilize the affected fossils and prevent any further pyrite decay. This is hugely important to ensure the survival of the museum's fossil collection for the future, especially given the importance of many of the fossils in our collection.

That's where you come in. We would like two volunteers to help us cut to size and seal the packaging that these fossils will be placed in to conserve them. This will not require any specialised skill or knowledge, and will simply involve cutting the material to size with scissors or a scalpel and sealing the sides with heat press so that the packaging is air tight, protecting the fossil inside from changes in humidity. In doing this you will be aiding the conservation of the museums fossil collection for the future.

During the project we will be asking you for suggestions on how we could streamline things, as the museum is hoping to speed up the process and provide training to other institutions.

Timing and commitment

The days available are Tuesday (2 people, approx. 10am-5pm) and Thursday (1 person, approx. 10am-5pm). We are hoping to start in early August and continue for an initial period of 4 weeks.
Coffee/tea will be available in the staff common room for breaks, and if you would like to use this room to eat a packed lunch this is also fine.

Ideal candidates will have the following interests and experience:

If you are interested in the conservation of museum collections, then this role is ideal as you will be helping to ensure the protection of many vulnerable specimens. We would prefer a volunteer who is accurate and precise, who is careful when handling fragile objects and who does not mind repetitive tasks, and who will not suffer discomfort after using scissors or cutting tools for long periods of time. This project may particularly appeal to those who already have an interest in fossils, as you will be able to work within the collections and see many different specimens.
The project may well be of interest to people who have worked on production lines using sealing equipment or cutting textiles, and those who have good knowledge of chemical processes.

Training

- You will be taken through the whole process from surveying to the final bagging process.
- We will show you how to make the packaging to our desired specifications
- We will train you to use the heat press safely and effectively
- You will receive specific instructions for each process.

Benefits for participating in this project

- Seeing 'behind the scenes' in the museum, including other parts of the Earth Collections.

- Gaining experience of working with our collections, and learning about specimen conservation.

- Helping us to preserve our fossil collections for the future.

- Meeting other volunteers and museum staff.

Volunteer expenses

We may be able to offer up to £4 per session for travel expenses if required.

Please submit your applications asap. In your application email please state why you would like to work on the project and why you think you are a suitable candidate.

The project is likely to be oversubscribed so please do not be disappointed if you are unsuccessful.

THE DENDERMONDE MAMMOTH: FIGHTING PYRITE DECAY AND THE PRESERVATION OF UNIQUE PALEONTOLOGICAL HERITAGE

by Anthonie Hellemond [1,2]

Hellemond, A. 2019. The Dendermonde Mammoth: fighting pyrite decay and the preservation of unique paleontological heritage. *The Geological Curator* 11 (1): 55-31.

The Dendermonde mammoth is a unique skeleton of a woolly mammoth (*Mammuthus primigenius*) which was found between 1968-1969, in the area around the city of Dendermonde (Oost-Vlaanderen - Belgium). This 29,000 year old skeleton was mounted in 1975 by its finder Hugo De Potter in the attic of the '*Vleeshuismuseum*'. The skeleton consists of ca. 74 original elements. Some of these elements originate from the Hofstade collection of the Royal Belgian Institute of Natural Sciences in Brussels (RBINS).

Since 1990 the skeleton has not been chemically treated and no monitoring of temperature or relative humidity took place. As a result of years of exposure and lack of any treatment, the bones of the Dendermonde mammoth were covered with a thick layer of dust and affected by pyrite decay. The skeleton was showing several visual outbursts of pyrite blooming out of the fossilised cartilage as well as numerous desiccation cracks. By the end of March 2017 the Belgian Paleontological Association (BVP), the Royal Belgian Institute of Natural Sciences (RBINS) and the city museum of Dendermonde (Stedelijk museum Dendermonde) decided to restore the skeleton in order to preserve an important piece of Belgian paleontological heritage.

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The discovery

In the historical Belgian city centre of Dendermonde (French: *Termonde*), we find the city's history (including natural history) museum called the "Vleeshuis" museum (the house of meat merchants). It is located in one of the most authentic sandstone buildings in the main market square of "Dendermonde" (a province of East-Flanders). Inside the majestic wooden attic of the museum, the city's oldest resident watches over the collection, which is packed with fossils and artefacts from the last ice age and prehistory. When walking up the impressive stone stairs that lead to the attic, visitors will encounter the paleontological pride of the "Dender" valley (the river flowing through Dendermonde). When we take a closer look at the information signs, we learn that this mammoth was found between 1968 and 1969 by Mr. Hugo Depotter, who also built the framework in 1975. The missing bits have been completed with fossils from the Hofstade collection from the Royal Belgian Institute of Natural Sciences in Brussels (RBINS) (Mourlon, 1909). In 1978, samples from the enamel of the molars were carbon dated to determine the absolute age of the mammoth skull (Vanhoorne *et al.* 1978).

Before March 2017, the skeleton was in a rather untended state. Due to the lack of conservation over the last 20 years, the poor climatological conditions under the roof and the absence of any interest by the general public, the mammoth had lost its appeal.

Pyrite decay

As a result of years of exposure and lack of any treatment, the bones of the Dendermonde Mammoth were covered with a thick layer of dust and attacked by pyrite decay. The skeleton was showing several visual outbursts of pyrite blooming out from the fossilised cartilage, especially the left shoulder blade (scapula) and right radial bone (radius), were heavily attacked by the typical grey-yellowish sulphur powder (Figure 1). This powder is the result of unstable pyrite bounding with oxygen atoms in the air. The reaction itself goes through different complex stages and eventually ends with the formation of $FeSO_4$ (iron sulphate) and SO_2 (sulphur dioxide). When dealing with a high relative humidity in the storage area, the water particles will cause the formation of H_2SO_4 (sulphuric acid).

The simplified chemical reaction goes as follows:

$4FeS_2 + 13O_2 + 2H_2O \rightarrow 4FeSO_4 + 2H_2SO_4 + 2SO_2$

(Pyrite) + (Oxygen) + (Water) -> (Iron sulphate) + (Sulphuric acid) + (Sulphur dioxide)

It is of the utmost importance that the influence of both water and oxygen, in combination with unstable pyrite, should be counteracted (Shinya and Bergwall 2007). The reaction itself not only leads to the formation of corrosive products such as the sulphuric acid, but also comes with a volume expansion. This expansion is the main reason why the bones will eventually lose their internal structures and disintegrate (cf. Larkin 2010). Aside from pyrite decay, the Dendermonde Mammoth also showed a large amount of desiccation cracks, as a result of the high variation in temperature. Such variations will also contribute to the fragility of the specimens, which will broaden the contact surface for oxygen and moisture, and keep the reaction mechanism going. It would be easy to blame the storage conditions, since the mammoth is displayed directly under the wooden structure of the roof. However, we should also bear in mind that the former treatments of the fossil bones were carried out rather superficially and most internal cavities did not benefit from any previous treatment. We also noticed visual signs of desiccation in the enamel of the molars. Specimens that suffer from pyrite decay, without initial visual signs of unstable pyrite blooming out of the internal structures, can also be affected. This effect can be related to chemical cross contamination and the Dendermonde Mammoth clearly suffered from it. The chemical cross contamination was clearly visible on both the bones and metal framework, where the sulphuric acid started to attack inert materials. The restoration project The Belgian Paleontological Association (Belgische Vereniging voor Paleontologie) took the initiative to set up a restoration project with the cooperation of the Royal Belgian Institute of Natural Sciences (RBINS) and the Museum department of the city of Dendermonde (Stedelijk Musea Dendermonde). The goal was to restore the entire mammoth in just one week, with a diverse team of experts. All bones had to be treated and restored before mounting them on the metal frame.

Treatment

To treat all the bones in an equal way, we had to find an effective method that was both time saving and cost reducing. Since the restoration team consisted of both professional conservators and citizen scientist with little experience, an easy-to-learn, step-by-step plan allowed us to tackle both complex and simple operations at the same time. This allowed us to treat every bone in a short amount of time while also focusing on the highly affected ones. For the basic treatment, following steps were needed. The first step consists of removing all visible pyrite and dust in a controlled environment. This can be done by using needles, scrapers, scalpels and toothbrushes (Figure 2). An experienced preparator will sacrifice only a small amount of original bone material during this first step. The amount of visible pyrite is an indication of the amount of fossil bone that has already disappeared through pyrite decay. It is recommended that the pyrite powder is removed while working under an extractor. This will prevent any corrosive airborne elements to wander around the room and be inhaled by the preparator. Personal protection throughout the entire process is important and very much so during this first step. Removing pyrite decay releases quite a pungent and unpleasant sulphuric smell and, without any protection, will irritate the throat and lungs. It is recommended that latex gloves and a surgical mask are worn when cleaning the bones with ethanol (to remove dust) and afterwards to remove the pyrite. Latex gloves will prevent any reaction with sulphuric acid, which will irritate the skin.

During the second step, the fossil bones are treated with a (mono)ethanolamine thioglycolate solution (Figure 3). This redox reaction will neutralise the unstable pyrite, which, in turn, will be washed away with pure alcohol (ethanol or methanol). Usually a 2% to 5% solution of (mono)ethanolamine thioglycolate with ethanol (EtOH) or isopropyl alcohol (IPA) is used. The first stage is to immerse the bones in the solution for about one hour. The pyrite inside the bones will react with the solution, turning it dark red and even purple. We change the solution every hour for the following three to four hours or until no change in colour occurs. This means that the pyrite has been stabilised. After this treatment, it is important to remove all traces of (mono)ethanolamine thioglycolate, by rinsing the bone(s) with ethanol (EtOH) or isopropyl alcohol (IPA) (Figure 4). During this process, it is important to keep an eye on previous restorations based on reversible glues. By using solvents, previously used adhesives can loosen or break. It is also important not to damage or alter the original patina of the bones by letting them dry too long immediately after the treatment. There are some downsides to the use of (mono)ethanolamine thioglycolate. One of the main problems is that this method is very time consuming and only works well with small bones. For the massive parts of the skeleton (like the skull, trunks or shoulder blades), we suggest the use of the solution locally by using syringes and tinfoil to prevent the solution from evaporating. Immersing these large bones in containers would be too expensive and impractical. In this

Figure 1. Pyrite decay on the right radial bone (radius) of the Dendermonde Mammoth. (© E. Coolen)

Figure 2. Removing pyrite powder with a scalpel on the right radial bone (radius) of the Dendermonde Mammoth.

Figure 3. (Mono)ethanolamine thioglycolate treatment. (E. Coolen 2017)

case, the procedure entailed treating the visual outbursts of pyrite disease by injecting the solution into the massive parts of the skeleton (e.g. cranium, tusks). Prior to the injection we make sure that all the cracks and fissures in the area are filled with a neutral calcite paste to avoid the solution leaking out of the bones. We let it sit for about three hours while wrapped in tinfoil. When we start to rinse, we make sure to remove the calcite paste and collect the ethanol or isopropyl alcohol in containers under the treated area.

When we reach the third step, all unstable pyrite will by now have been treated, but this does not mean that in the near future there won't be any outbursts of pyrite decay. The chemical reaction mechanism is still going on and the next step is to interfere with the reaction itself (Godefroit 2008; Larkin 2010). The best way to do this is to cut off the influence of oxygen and water, by treating all the bones with a polyvinylacetate or acrylate solution (Figure 5). Therefore, we use products such as: Mowilith™, Osteo-Fix™ (Degalan 4792L) and Paraloid B-72™. For the mammoth we used Mowlith™ beads which are dissolved in acetone. By applying this solution to the bones, the polyvinylacetate solution will penetrate deeply into the internal structures of the bone, where the acetone will evaporate and cover the bone with a strong film. This film will temporarily cut off the contact with the air and, at the same time, strengthen the internal structures of the bone itself. It is important to execute this treatment in an aerated (ventilated) environment and, at the same time, use latex gloves and oxygen masks to protect yourself from the acetone fumes.

During the fourth step, after the internal and external treatment of each bone, we can concentrate on the treatment of the desiccation cracks (Figure 6). After the polyvinylacetate treatment, each bone will have a glossy look and will feel a lot more solid than previously. Unfortunately, there is not a lot you can do about desiccation cracks. The most common solution is to fill up the cracks with a (pH) neutral modelling clay (Fimo™ Basic Air calcite paste), which will not react with the remaining (stabilised) pyrite or the polyvinyl film. After applying the paste, it is important to make a decision about what colour you want to apply to it. Since the Dendermonde mammoth is part of a public exhibition, we chose to hide all restoration work by covering it with pigments resembling the original patina of the bones. We used a completely different approach when dealing with a collection that is meant for scientific research, where all restoration steps should be visible for everyone who would like to do research on the specimens. The pigment is fixed on the bone with Paraloid b72™.

The fifth and final step is to reassemble the bones on the original metal frame, without damaging them. In the case of the Dendermonde Mammoth, we used metal wire to secure the position of each bone. After positioning, there is the possibility to fix the last scratches with calcite paste and pigment (Figure 7). The metal framework also received an additional checkup and a new layer of paint. We also replaced (welded) two metal rings who were corroded by the pyrite decay.

Figure 4. Vertebrae of the Dendermonde Mammoth after being rinsed in ethanol (EtOH). The ethanol will remove the last traces of (mono)ethanolamine thioglycolate.

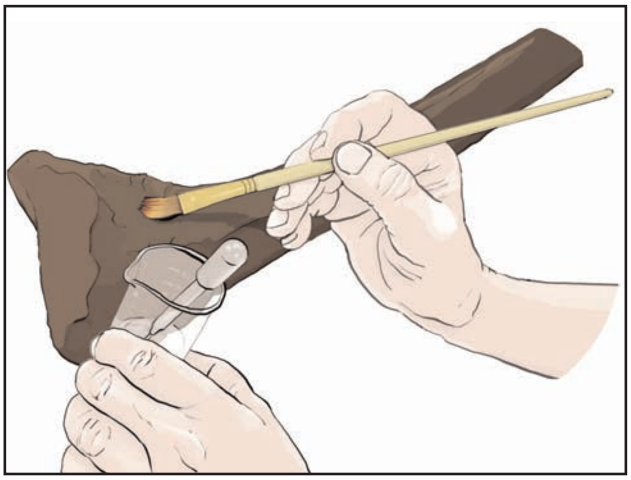

Figure 5. Polyvinyl acetate treatment. (© E. Coolen)

Figure 6. Filling up the desiccation cracks with white calcite paste.

Figure 7. Mounting and colouring the bones.

Conclusion

Pyrite decay is a severe problem in many paleontological collections and can spread itself from one specimen to another, causing a lot of damage to a (scientific) collection. External factors, such as variation in relative humidity and temperature, can play an important role as accelerants within the chemical reaction. When asked how quick pyrite decay can affect a collection, there is no standard answer. Within a confined space, where a collection is stored, the sulphuric smell might be the first indication that the reaction is going on. The reaction itself takes place on a microscopic level and, based on research, seems to occur often when dealing with framboidal pyrite (Figure 8). It is necessary to monitor and react in time by all possible means, when faced with a visual sign of pyrite decay (Pfretschner 2000).

Finally, treatment should never be seen as a permanent cure for pyrite decay, but should be repeated on a regular basis, and certainly when faced with a visual outburst of pyrite decay on fossils. Only then is there a guarantee that a collection can last for several generations.

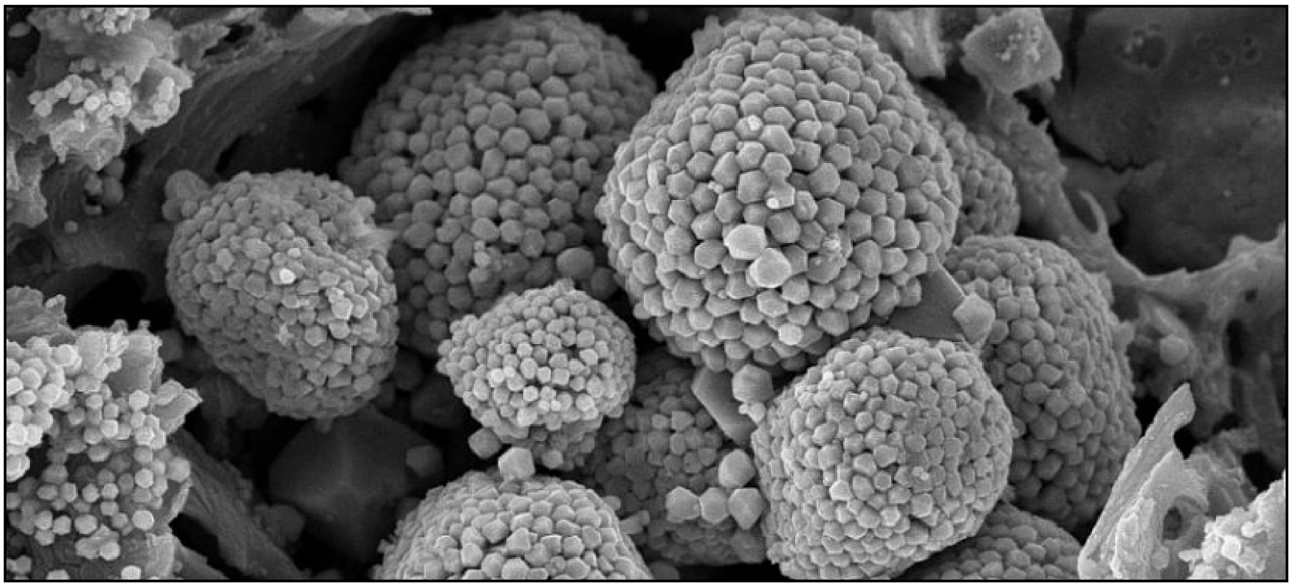

Figure 8. Framboïdal pyrite - under a scanning electron microscope (Lojen 1999).

Successful Collaboration

As a result of this successful collaboration, visitors of the museum are once again able to meet the 'oldest' resident of the city of Dendermonde restored to its former glory. This project is the perfect illustration of how federal institutions, local government, and scientific organisations took action and worked together for the preservation of national scientific and paleontological heritage in times when the financial means for scientific research are scarce. We can apply an important lesson to our own collection based on this restoration project. In the first place, we should acknowledge the importance of local paleontological history, and try to contribute to its preservation and scientific study by maintaining an open collection for scientific research, and invest in decent preservation of your collection.

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PYRITE DECAY - INTO THE GREAT UNKNOWN

by Christian Baars

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More than 200 years of research have brought us little closer to understanding, let alone controlling, pyrite oxidation in geological collections. This appears paradoxical, because thousands of papers have been written on the deterioration of iron sulfides by geochemists, engineers and conservators. But whilst reaction products and pathways are characterised well, the causes of deterioration of different types of iron sulfide specimens in geological collections remain elusive. To make matters even more complicated for the museum conservator, published guidelines for the management of such specimens are patchy and often contradictory. Currently available condition assessment methodologies are barely suitable for routine monitoring of large collections, results of specimen monitoring exercises are not necessarily replicable, and, in the absence of guidance on suitable storage conditions, triggers for, and suitability of, conservation actions are difficult to determine. A new approach is required to end the guess work and add some substance, based on evidence, to the collection care of geological collections in museums. This paper does not answer these questions but introduces a framework for a research agenda that would underpin a robust approach to the delivery of preventive conservation of geological collections. This includes a definition of what kind of material change in minerals constitutes damage; categorisation of damage/change; development of a protocol for routine condition assessments; the definition of an adequate storage environment; and testing rigorously the suitability of conservation treatments.

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Introduction

> "But alas! One disagreeable Circumstance attending a considerable Part of the Fossils here collected, is, that they are so much impregnated with pyritical Matter, that after being for some Time placed in a Cabinet, the Salts thereof shoot and entirely destroy them. Happy would it be, could some certain Remedy be discovered whereby this Accident might be prevented. The Loss of many valuable Specimens by this Cause, together with his Distance from any inquisitive and able Naturalists, at last induced the Author to dispose of his whole Collection to Ingham Foster, Esq; Merchant of London, where it now forms no inconsiderable Part of that Gentleman's very valuable Cabinet."

Since Edward Jacob's cry for help, cited by Torrens (1977) precisely 200 years later, there has been a dearth of knowledge in subjects that would help collectors and museums care for 'fossils impregnated with pyritical matter being destroyed by salts shooting' and preserve notoriously unstable iron sulfide specimens. Pyrite is the most stable and insoluble iron sulphide mineral, but when exposed to O_2 and other oxidants, it oxidises. Understanding the oxidation of pyrite is an important environmental problem in iron and sulfur cycling as it occurs in freshwater and marine systems as well as acid mine areas. Iron sulfides are frequently found in mines and their oxidation can cause significant environmental damage, which motivated intensive research by the mining industry. On a global scale almost all acid rock drainage, whether natural (as in the development of massive or disseminated gossan, the oxidized equivalent of massive or disseminated sulfide, respectively) or related to anthropogenic activities (as in the generation of wastes from mining and mineral processing) can be traced to the oxidation of pyrite (Jambor *et al.* 2000). The oxidation of pyrite to sulfates was reviewed by Nordstrom and Alpers (1999) and Rouchon (2012). Although the details of iron sulfide decay mechanisms are still under investigation (Murphy and Strongin 2009) most authors now agree that the decay involves the oxidation of sulfide into sulfate species. Sulfur is oxidized while iron remains Fe^{2+} when released into solution (Rouchon 2012). The sulfur oxidation is an electrochemical process involving a series of reactions (Jambor *et al.* 2000 pp. 319, Chandra and Gerson 2010, Schoonen *et al.* 2010, Heidel and Tichomirowa 2011):

1) a cathodic reaction occurs with an oxidant species (mostly O_2 or Fe^{3+}) at the surface of mineral grains

that removes one electron;
2) transport of a charge from an anodic site to the cathodic site enables the replacement of the lost electron;
3) a sulfur interaction with oxygen or water leads, on the anodic site, to the formation of sulfoxy species (Rouchon 2012).

The oxidation process does not occur randomly across the surface but instead is initiated at specific locations and then spreads outward from these initiation points to form rather large oxidized patches coexisting with unoxidized parts of the surface (Eggleston *et al.* 1996). Sulfide oxidation is accelerated as pH decreases, because mineral solubilities and metal concentrations increase with decreasing pH (Jambor *et al.* 2000).

Those sulfide oxidation reactions occur in the presence of liquid water, frequently resulting in acid mine effluents, following two principal pathways:

Aerobic:
$FeS_2(s) + 7/2O_2 > Fe^{2}+ + 2SO_4^{2}- + 2H+$

Anaerobic:
$FeS_2(s) + 14Fe^{3+} + 8H_2O > 15Fe^{2+} + 2SO_4^{2-} + 16H^{+}$

Hydrogen ions are a major product of pyrite oxidation, and oxygen isotope data indicate that the oxygen atoms in sulfate ion come from water (Luther 2016 p. 384). Thus, a dramatic decrease in pH occurs in many environmental system, and microbial Fe(II) oxidation is necessary to sustain the oxidation. For example, in acid mine areas where pyrite is a constituent in coal, the pH can actually be near or below 0.

Under 'dry' conditions in museum collections, 'spontaneous' growth of sulfate minerals has long been known to occur as alteration products on pyrite and marcasite specimens (Workman and Rader 1961, Grybeck 1976, Wiese *et al.* 1987, Luzgin 1990, Blount 1993). The oxidation products include $Fe(OH)_3$, goethite (FeOOH), sulfuric acid and efflorescence of various hydrated sulfates (for example, ferrous sulfate ($FeSO_4$) and polyhydrated iron sulphates such as copiapite ($Fe^{2+}Fe^{3+}(SO_4)6(OH)_2 \cdot 20(H_2O)$), fibroferrite ($Fe^{3+}(SO_4)(OH) \cdot 5(H_2O)$), melanterite ($Fe_2O_4 \cdot 7(H_2O)$)) (Wang *et al.* 1992). Chalcanthite and melanterite are potential oxidation products of pyrite (Jambor *et al.* 2000 pp. 321). Many authors have observed paragenetic sequences of metal-sulfate products of sulfide oxidation with decreasing hydration states; for an overview see Jambor *et al.* (2000 pp. 339). The extent of the involvement of anaerobic bacteria in the oxidation of specimens under museum store conditions has not yet been investigated.

Deteriorating minerals

Preservation of specimens in their original, as-collected state is therefore a common problem for museums. Studies by Morth and Smith (1966) and Smith and Shumate (1970) showed that the oxidation rate of pyrite increased steadily as a function of relative humidity (RH). Consequently, potential conservation treatments of deteriorating pyritic specimens centre on excluding contact of specimens with water vapour and oxygen (e.g. Brunton *et al.* 1984, Waller 1987, Costagliola *et al.* 1997, Newman 1998, Larkin 2011, Baars 2013). The rationale for the development of collection care guidelines (Table 1) must be understood with this background in mind.

By the 1980s some detailed guidance was available to advise museums on the appropriate storage of pyritic specimens. But iron sulfides are not the only minerals that are unstable under indoor environmental conditions. Other examples of temperature and humidity sensitive minerals include chalcanthite

Material	Temperature [°C]	Relative Humidity [%]	Reference
Pyrite		< 60	Howie 1978
Pyrite		30	Howie 1992
Pyrite		~ 30	Waller 1992
Pyrite/marcasite	16-22	< 60	US National Park Service (Conserv O Gram) 1998
Pyrite		< 30	Hodgkinson & Martin (BGS) 2004
Pyrite		< 50	Shepherd & Tulloch 2007 (BGS)
Pyrite/marcasite		< 60	PAS 198:2012

Table 1: Recommended collection care guidelines for the preservation of pyritic specimens in geological museum collections.

Mineral species	Chemical formula	Reaction	RH [%]	T [°C]
Chalcanthite[1]	$CuSO_4 \cdot 5H_2O$	Deliquescence Dehydration	97 33	25 25
Marcasite[2]	FeS_2	Oxidation	unknown	metastable
Melanterite[3]	$FeSO_4 \cdot 7H_2O$	Deliquescence Dehydration	95 57	20 20
Pyrite[4]	FeS_2	Oxidation	unknown	<743
Pyrrhotite[5]	$Fe_{1-x}S$ (x = 0 to 0.2)	Oxidation	unknown	monoclinic form stable <254 hexagonal form stable >254

Table 2: Environmental vulnerabilities of some mineral species.
Notes: [1] - Collins and Menzies (1936), [2] - Craig and Scott (1976 p. CS-30), [3] - Waller (1992), [4] - Kullerud and Yoder (1959), [5] - Klein, Hurlbut and Dana (1985, pp. 278-9).

$(CuSO_4 \cdot 5H_2O)$ which deliquesces at 97% and dehydrates at 33% RH, both at 25°C (Collins and Menzies 1936) - values that may be reached museum stores. Melanterite $(Fe^{2+}(H_2O)_6SO_4 \cdot H_2O)$ is one of the most common soluble sulphate minerals formed in nature (Jambor *et al.* 2000). It has similar deliquescence RH to chalcanthite (Waller 1992; table 3). Metal sulfate salts occur most commonly in association with the oxidation of metal-sulfide mineral deposits (Jambor *et al.* 2000 pp. 321 and references therein). Approximately 10% of known mineral species have specific environmental requirements and therefore are susceptible to alteration when exposed to environmental conditions in the typical museum store (Waller 1992). Many of the simple salts are extremely sensitive to atmospheric conditions and change their hydration state, in many cases irreversibly, in response to prevalent temperature and relative humidity conditions (e.g. Keller *et al.* 1986, Waller 1992, Chou *et al.* 2000). Salts may deliquesce at their equilibrium relative humidity (RH), which is the RH of air that is in equilibrium with a salt solution. The deliquescence RH is the RH that functions as the line of demarcation between crystallization and deliquescence (Paterakis 2016), which may affect some of the sulfide oxidation products. Chalcanthite deliquesces at 97% and dehydrates at 33% RH, both at 25°C (Collins and Menzies 1936) - values that may be reached in some museum stores. Melanterite is one of the most common soluble sulfate minerals formed in nature (Jambor *et al.* 2000). It has similar deliquescence RH to chalcanthite (Waller 1992; table 2). Metal sulfate salts occur most commonly in association with the oxidation of metal-sulfide mineral deposits (Jambor *et al.* 2000 pp. 321 and references therein) and may therefore be anticipated to be products of pyrite decay.

In addition to inappropriate temperature and relative humidity, pollutants may contribute to the deterioration of minerals. Bob King recommended museums use wooden drawer cabinets for the storage of mineral collections to buffer against environmental fluctuations, whilst noting the problems of 'slow emanation of acid vapours' from wood which were 'intensified by high ambient temperature and RH' increasing greatly the 'hydrolosis (sic) of hemicellulose in timber to acetic acid'; King's solution was to use 'well-seasoned mahogany' or 'naturally-seasoned or old deal' as an alternative to young wood, composite wood and softwoods (King 1986). This advice was founded on the mistaken belief that the emission of organic acids from wood decreases or even ceases with time, which we now know not to be true (Gibson and Watt 2010, Risholm-Sundman *et al.* 1998). Carboxylic acids are a ubiquitous indoor pollutant in museums (Grzywacz and Stulik 1993); sources are mainly wooden compounds or other building materials (for example, Schieweck *et al.* 2005, Gibson and Watt 2010). Hardwoods emit especially high concentrations of acetic acid due to the large amount of acetyl groups present in hardwoods (Risholm-Sundman *et al.* 1998).

Relatively little, compared to metals and ceramics, is known at present about the effects of carboxylic acids on minerals even though calcium acetate efflorescence on minerals was attributed as early as 1931 to their exposure to acetate as a result of storage in wooden cabinets (Taboury 1931). A hydrated calcium chloride nitrate acetate efflorescence was identified on a Jurassic ammonite in the Natural History collection of the British Museum (Howie 1978). Waller *et al.* (2000) investigated pollutants generated by geological specimens in museum storage, focussing on the effects of both cabinet materials and minerals on types and levels of pollutants detected; acetic acid equivalent concentrations were in the order of between 0.8ppm and 6.5ppm. Cabinets with apparently low levels of air tightness exhibited little difference between room and cabinet pollutant concentrations except in cabinets containing clusters of pollutant emitting or scavenging mineral specimens, whereas in cabinets with apparently greater levels of air tightness pollutant concentrations related more directly to contents and cabinet materials (Waller *et al.* 2000). However, at the time, the authors did not measure the air tightness of the different cupboards examined (Robert Waller pers. comm.) which must be taken into account when interpreting the results of that study. Pollutant concentrations in mineral storage cabinets are apparently more dependent on cabinet materials and mineral species than on room air concentrations, with some minerals being either emitters or absorbers of pollutants (Waller *et al.* 2000). Measurements of carboxylic acids in room air in National Museum Cardiff's mineral store indicated the presence of a mean acetic acid concentration of 1625µgm^{-3} (0.653ppm) and mean formic acid concentration of 90µgm^{-3} (0.047ppm) prior to the installation of a new fresh air ventilation supply (unpublished data), which is in the lower range of Waller *et al.*'s (2000) measurements within wooden cabinets. It is currently unclear, however, how much the high concentrations of carboxylic acids detected at National Museum Cardiff contributed towards damage observed on mineral specimens.

Whilst there is circumstantial evidence that high concentrations of carboxylic acid emitted by wooden storage furniture may contribute to the deterioration of minerals, the effects on sulfides in particular are under researched; it is also not known whether threshold concentrations exist above which reactions between organic air pollutants and stored minerals are more likely to occur.

Notes on unresolved pyrite deterioration questions

The very specific environmental requirements of different mineral species - at least those that are known - indicate that the collection care guidance available for geological collections (Table 1) is entirely inadequate. Even a satisfactory definition of what constitutes an 'appropriate' storage environment is currently not available. The closest characterisation of 'appropriate' is by Duyck (2012) who suggests that a storage space must be 'suitable' in the sense that "space must be large enough to accommodate the existing collection as well as the projected growth (…) over the next 10 years. (…) Raise cabinets (…) so that they are 4-6 inches off the floor". A more practical suggestion is that an appropriate storage environment for geological collection is one that does not cause any unwanted chemical or physical changes to specimens. What this means for temperature, relative humidity, pH, bacteria, gaseous pollutants, reactive dust and other parameters potentially affecting the deterioration of sulfide minerals is an as yet open question.

The debate over what constitutes an appropriate storage environment for pyrite and other minerals is also affected by what we mean by damage. The concept of damage is highly subjective: it is dependent on observers and context, and influenced by values (Ashley-Smith 1999). It is now understood that damage cannot be defined objectively (Munoz Vinas 2002). Leaving all other values (Baars 2011) aside and focussing 'simply' on the difference between research and aesthetic value, if a mineral specimen has scientific value and is used for scientific purposes such as chemical analysis, no amount of chemical change is acceptable. Yet if a specimen is used for its aesthetic value some change may be acceptable, so long as the specimen does not become unstable. Robb *et al.* (2013) explained that, for the mineral curator, the value of geological specimens, in particular, can be linked to contextual information such as collector, locality, collection date and so on, rather than the integrity of the specimen itself.

The concept of damage to geological specimens was explored by Baars and Horak (2018). Fundamentally, damage signifies a change in the material state of an object. Not all change can be considered damage in the sense that it would lead to a loss of significance (Ashley-Smith 1999). Ashley-Smith (1999) explored the concepts of 'acceptable damage', 'perceptible change' and their relationship to object value. Occasionally, the determination of unacceptable change is straight forward. Unacceptable change is demonstrated unequivocally when a vase is knocked of its plinth and breaks into many pieces-a case of 'unintentional visitor participation' (Blühm 2016). Unacceptable change is less clear in the slow degradation of pyrite, as the process of oxidation is initially invisible to the naked eye but may be entirely measurable using appropriate instrumentation.

Objectifying the concept of damage as being a function of unacceptable change dependent on agents of change opens up the opportunity for decoupling the value function from the change function (Strlic *et al.* 2013). This opens the door to a separation of value from parameters that can be measured. A material response to an agent of change is often affected by dose, for example, a threshold concentration of a pollutant, or impact, and may be measurable and quantifiable. A very useful tool to establish a dose response is that of the 'no observable adverse effect level' (NOAEL; Tetreault *et al.* 2003): the highest concentration of a pollutant before it produces any observable adverse effect. The concept of NOAEL pragmatically circumvents the notion of 'damage' and it appears prudent to apply this to geological collections as a way of using objective criteria to assess change.

The practical implication of defining exactly what we mean by damage to pyrite or pyritic specimens is that it should become easier to undertake condition assessments. How do we undertake a condition assessment if there is no consensus about what constitutes 'damage'? Observable changes that are a result of pyrite oxidation may manifest themselves as smell, tarnishing, cracking and the development of efflorescence. These are tangible processes that are measurable and perhaps even quantifiable. The important step would be to develop a methodology that would allow quick, cheap and easy quantification of some of these processes to inform an objective assessment of specimen condition. Such a methodology would also presume minimal data processing and maximum automation and be reliable, easy to use, cost-effective and deliver reproducible results.

Present condition assessment methodologies rely heavily on visual examination of specimens. The results of such assessments may therefore suffer from poor comparability, especially so if undertaken by different people, due to 'intersurveyor differences' (Taylor 2005). Objective protocols (that is, those that focus on quantification of chemical and physical changes) are yet to be developed but would clearly improve the consistency of condition assessments. A non-invasive method would be preferred to increase the speed of condition checking and leave specimens unchanged to preserve their integrity. Odin *et al.* (2014) agreed that future research on geological specimens would be helped by the development of a methodology capable of characterising and quantifying the mechanical damage to small (2-3cm) samples. Potential targets of analysis may be the products of pyrite oxidation reactions, such as gases and various sulphates, or changes in specimen weight, reflectance, or the amount and size of micro-cracks.

Historical attempts at preventing pyrite decay included the neutralization of acid oxidation products, removal of badly decayed areas, and thorough drying and impregnation with an 'impermeable' consolidant. Howie (1977a) provided an overview of preventive storage efforts such as coating, impregnation or immersion, but questioned their effectiveness in preventing pyrite decay when reporting that specimens previously conserved by impregnation with various resins, as well as those treated with bactericides, were found to start deteriorating when transferred from a store with RH of 40-45% to a new facility at 60-65% RH (Howie 1977b). It is also the experience of the author that synthetic coatings such as polybutyl methacrylate (Bedacryl) are not effective at preventing the deterioration of pyritised ammonites (Baars 2013) and may actually increase the susceptibility of affected specimens by sealing in corrosive gaseous deterioration products, in essence creating the 'perfect' micro environment for further deterioration. Old coats of varnish or lacquer frequently have to be removed by using an air abrasive with sodium bicarbonate powder (Cornish and Doyle 1984) or careful dissolution (Baars 2013).

More recently, pyritic specimens have been sealed in barrier film which is one way of separating vulnerable specimens from inappropriate environmental conditions and creating a more suitable micro-environment (Larkin 2011). Use of barrier films is frequently in conjunction with prior treatment of specimens for removal or neutralisation of oxidation products (Baars 2013), and inclusion of hygroscopic sorbents and oxygen absorbers inside the micro-environment (Day 2005). Storage in micro-environments increases the physical footprint of each specimen in the collection and has maintenance consequences. There is anecdotal evidence from the collections at National Museum Cardiff that repackaging pyrite specimens in micro-environments may cause an acceleration of the deterioration of specimens for reasons that are currently unknown. It is possible that some sealed bags or pouches are not as tightly sealed as intended - either because the barrier film has become punctured, or because one of the seals is faulty. Alternatively, if an oxygen scavenger was introduced into the micro-environment, and pyrite oxidation was mediated by bacteria, it is conceivable that the proportion of aerobic to anaerobic bacterial populations shifts in favour of the latter, in which case pyrite oxidation may continue unhindered despite the change in environmental conditions.

Triggers for conservation intervention during pyrite decay are poorly defined and often relate more to capacity of conservation staff than to the collection care demands of specimens; this applies to whether specimens are stored in the main collection run or in micro-environments. One issue with sealing pyritic specimens in barrier film is that specimens are less accessible. This means that even routine condition assessments are difficult to undertake without breaking the seal or removing specimens from their micro-environments, which potentially results in environmental fluctuations and, consequently, unwanted changes to specimens. This practice also increases the amount of time and resources that have to be allocated to undertaking condition assessments. One potential solution would be the development of a protocol that would allow the non-invasive remote analysis of specimens or reaction products that may be the result of chemical deterioration through the protective barrier film. Such a protocol has not yet been developed.

Conclusions

A conference was held in 1986, organised by the Geological Curators Group, to discuss the conservation of geological materials. In the conference proceedings, published as a special edition of the *Geological Curator*, Jonathan Ashley-Smith, whom, as my mentor, I have immeasurable respect for, wrote that he considered the conservation of geological material 'not too dissimilar' from that of decorative arts. In his view, the environmental control of collection was 'fortunately (…) embarrassingly simple' and a 'matter of common sense' (Ashley-Smith 1987). The brief overview in this current paper, combined with a more detailed analysis by Baars and Horak (2018), indicates that perhaps things are not as straight forward as Ashley-Smith - and other authors - expected 30 years ago. In fact, there is sufficient evidence to dispel the myth that geological collections are inherently stable and require fewer resources than other types of museum collections.

Instead, a considerable proportion of mineral collections demand a high level of attention and maintenance, and precise environmental and pollution-related considerations. But despite centuries of research on pyrite decay there is a catalogue of questions about the conservation of geological materials, and, in particular, pyritic specimens requiring urgent attention:

- how to categorise damage in geological collections,
- how to assess, measure and analyse any deterioration objectively and with limited resources in museums, resulting in a standard protocol for condition assessing geological specimens,
- what constitutes an 'ideal' storage environment,
- how to ensure an adequate storage environment free of airborne pollutants, and
- what conservation treatment to undertake if any deterioration is detected.

It is difficult to determine conservation triggers and priorities without this knowledge. The prerequisite of any meaningful collection care is a comprehensive definition and consensus about what we mean by 'damage' to minerals and what level of damage to specimens is acceptable. This would then allow the development of a workable protocol for the objective, non-invasive and routine assessment and monitoring of the condition of any geological collection for potential changes. Whether change to a specimen, once detected, would trigger a conservation response relies on knowledge of the stability limits and reactivity of minerals to environmental factors. These questions cannot be answered through case studies alone but require systematic research and experimentation. A project is currently underway at National Museum Cardiff, in partnership with the University of Oxford, to elucidate some of these questions.

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THE EXCAVATION OF HIGH ARCTIC, LATE JURASSIC - EARLY CRETACEOUS MARINE REPTILES AND THEIR VIRTUAL AND MANUAL PREPARATION

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Roberts, A.J., Funke, M.LK, Engelschiøn, V.S. and J.H. Hurum. 2019. The Excavation of high Arctic, Late Jurassic - Early Cretaceous marine reptiles and their virtual and manual preparation. *The Geological Curator* 11 (1): 69-79.

The recent excavation of nearly 60 marine reptile specimens from the Slottsmøya Member, central Spitsbergen (Svalbard, Norway) straddling the Late Jurassic- early Cretaceous boundary, has led to the testing of numerous novel excavation techniques in the field and developed preparatory methods in the laboratory. Key results of this laboratory work show that the use of the adhesive Mowilith, a polyvinylacetate dissolved in alcohol, represents a good alternative to paraloid-type adhesives for temporarily stabilizing extremely fractured material during preparation. Permanent cyanoacryoloid adhesives used on the material in the laboratory have successfully stabilized the specimens from further deterioration, although thorough cleaning prior to the application is required for a lasting effect. Finally, we present the case study of a plesiosaur skull, where computed tomography is utilised to support further preparation of the specimen. Computed tomography images were used as aid to locate the borders of the bone material, allowing for more of the surrounding matrix to be removed without causing damage to the specimen. We show utilisation of computer tomography provides a virtual preparation alternative for particularly fragile specimens.

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Introduction

Eight seasons of extensive fieldwork performed by a joint group of researchers, students and volunteers largely based at the Natural History Museum, University of Oslo, Norway were conducted in the black shales of the Slottsmøya Member of the Agardhfjellet Formation in the central Spitsbergen Sassenfjord area between 2004 and 2012 (Figure 1). The excavations were a major part of the ongoing research by the Spitsbergen Mesozoic Research Group which include about 40 people from institutions in several countries, see a summary in Delsett *et al.* (2019). The excavations have yielded numerous skeletal remains of plesiosaurs and ichthyosaurs from several sites in about 20 km of hillsides containing the member (Druckenmiller *et al.* 2012, Druckenmiller and Knutsen 2012, Knutsen *et al.* 2012a, Knutsen *et al.* 2012b, Roberts *et al.* 2014, Roberts *et al.* 2017, Delsett *et al.* 2018, Delsett *et al.* 2017). The specimens from this member display different states of preservation and vary substantially in completeness, degree of deformation, surface erosion and mineralisation. The taphonomy and preservation of the specimens are described by Delsett *et al.*, (2016), and the mineralization and fluid inclusions by Kihle *et al.* 2012. Field seasons in the high Arctic (78º N) are short, as the localities are only snow-free for approximately four weeks a year. The fractured condition of the fossils offers multiple excavation and preparatory challenges, as numerous types of adhesives and encasing materials fail to work optimally under these conditions e.g. temperature between -5 - 10+ Cº complicated further by the presence of permafrost and moisture. As such, both new and old techniques have been tested during the excavation and preparation of these specimens, some of which could prove useful for planning future excavation and preparation of material from the Polar Regions. Here we present examples of the challenges experienced when excavating and preparing these specimens, as well as our solutions to surmounting them. All specimens excavated in this project are housed in the Natural History Museum, University of Oslo, Norway with the collection prefix PMO.

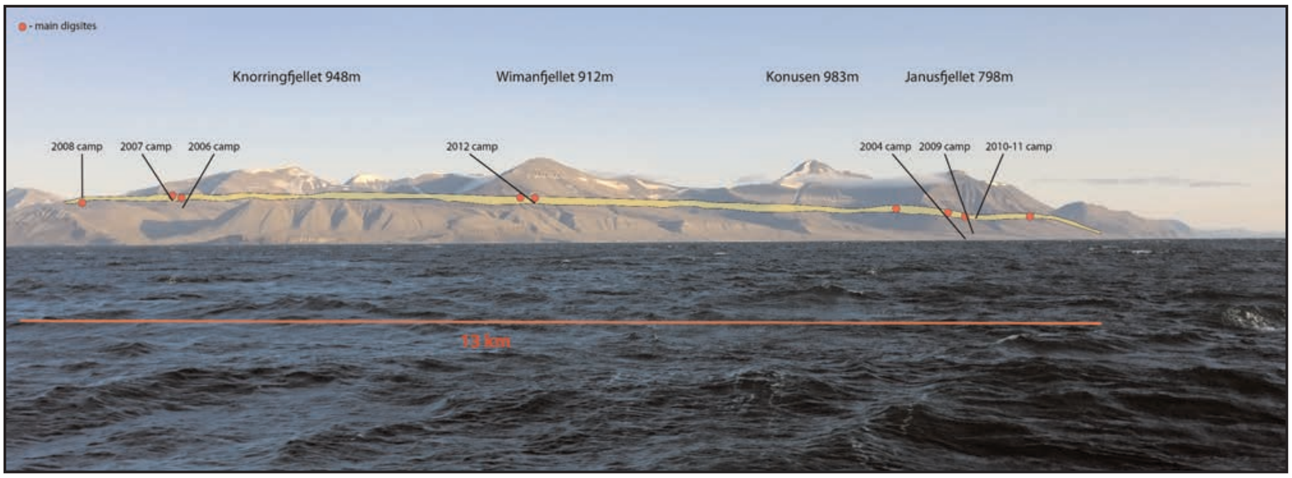

Figure 1. Photo of the field area with the Late Jurassic - Early Cretaceous Slottsmøya member marked in yellow and name of mountains, major excavations and campsites included.

Preservation

Marine reptiles found in organic-rich shale such as the Posidonienschiefer in Holzmaden (Germany), are usually compressed (Martill 1993 and references therein). The Slottsmøya Member is comparable with regards to the fine-grained matrix and the high degree of compaction, however, it displays a higher sedimentation rate (Delsett *et al.* 2016). As a result, many of the marine reptile specimens have not undergone compaction to the same extent as the fossils from the Posidonienschiefer. Research has indicated that the presence of early pore mineralisation (permineralisation) by barite ($BaSO_4$) and calcite ($CaCO_3$) in two stages could be responsible for the relatively three-dimensional preservation observed in many of the specimens (Delsett *et al.* 2016, Kihle *et al.* 2012). The documented presence of *in situ* cold seep carbonates in the upper section of the Slottsmøya Member (Hammer *et al.* 2011), could be the mechanism for the remobilisation of barite into the pore spaces within cancellous bone of the marine reptiles (Delsett *et al.* 2016).

The key difference between excavating and preparing vertebrate fossil material from high latitude versus lower latitude areas is how the specific climatic conditions affect the integrity of material. For example the presence of permafrost at about one meter depth, and when exposing the frozen shale it starts to melt and the quarries are turning into mud; the lack of vegetation in these mountains due to the harsh weather conditions and extremely high latitude (78^{o} N) exposes the fossil material to a high rate of climatic erosion and physical weathering; and due to the freeze-thaw processes in the active layer of the permafrost, most of the specimens have undergone congelifraction (fragmentation by freeze-thaw processes in the active layer just above the permafrost). The main types of preservation states for the Slottsmøya Member material are the following (Figure 2): (A) partially or completely in siderite nodules; (B) covered in secondarily formed gypsum and iron oxides in the black shales; (C) subjected to congelifraction, particularly in the black shales and (D) several of these states can occur simultaneously in the same specimen. In addition, some of the specimens that were found exposed on the surface have been subject to significant environmental erosion.

Excavation

During the excavation of the specimens, traditional excavation tools such as hoes, spades and jack hammers, as well as more unorthodox equipment such as chainsaws, were used to cut away the permafrost and expose the specimens. The first meter is usually melted and consists of a brittle paper-shale easy to remove, but then the excavation hit the permafrost in the shale. When exposed, no consolidation was added due to the frost and humid condition, only toilet paper (minimum 5-ply) was dampened with water to form a papier-mâché cover preventing moisture loss and creating a coherent, yet pliable barrier between the plaster and bone (Figure 3A). Attempts at using aluminium foil as a boundary layer caused significant damage to the specimens over time, as the aluminium foil disintegrated in the low pH environment of the pyrite-rich organic shale.

Plaster (Giluform 250) was used to make the jackets, coupled with inlaid burlap and metal rods to strengthen the packaging. This type of plaster works well in cold environments (range of approximately -5 to +5 C^{o}), although it requires to be hand-held in place along the undercut sides during the initial part of the hardening process (Figure 3B-C). The most crucial ingredient to ensure sufficient hardening was clean water with a minimal content of silt and clay particles. For small meltwater creeks, either a dam

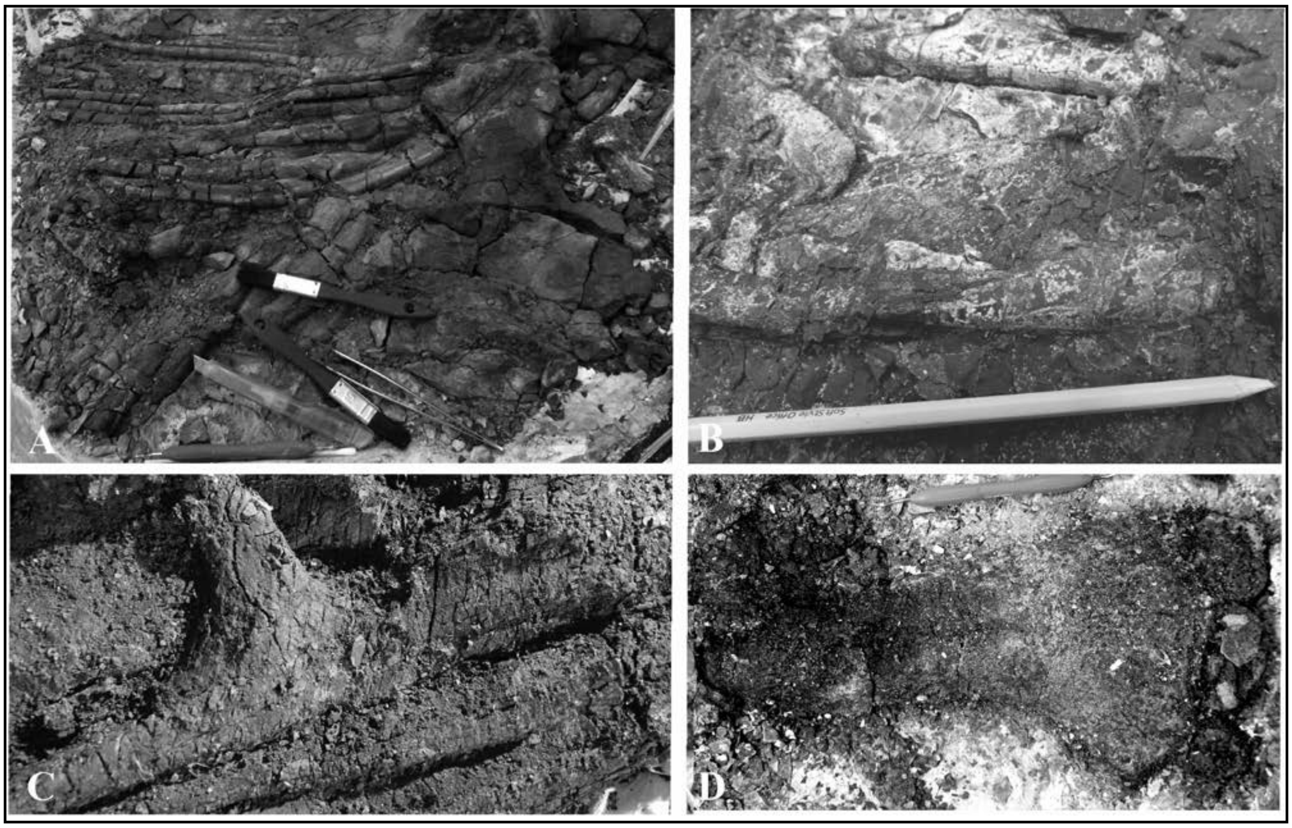

Figure 2: Different types of preservation in the Slottsmøya Member marine reptiles. A, Preservation in siderite-rich matrix in an abdomen of an ichthyosaur (PMO 222.669); B, gypsum-covered bone elements of an ichthyosaur skull (PMO 222.669); C, Extreme fracturing from freeze-thaw processes on an ichthyosaur skull (PMO 222.654); D, extreme fracturing from weathering and congelifraction and covering from gypsum flakes on a plesiosaur humerus (PMO 224.248).

for clearing the water was dug or large buckets were used where sediments were left to settle at the bottom from one day to the next. Alternative packaging, such as expanding polyurethane spray foam was also tried with less success. Due to the cold climatic conditions, standard foam did not expand and took at least 12 hours to set, and foam made for cold conditions only very slowly expanded and set. This was too slow for the excavation team, but the foam was used between the jackets as support during helicopter transport.

The area surrounding the specimen was first trenched, and subsequently undercut after the application of the top plaster jacket. Undercutting had to be undertaken carefully as the permafrost holding the shale together would start melting both from exposure to the atmosphere and due to the exothermic reaction of the plaster hardening. The thawed or thawing shales could therefore collapse into the trench. The specimens in their plaster jackets were separated from the ground using custom-made 0.5-1m long iron chisels. The chisels were driven in under the top jacket until they almost formed a floor supporting the brittle shale (Figure 3D-E). When they had been struck in place, rope was tied around the ends, enabling the jacket to be flipped manually (Figure 3D) and preventing the specimen and matrix from falling out of the bottom of the jacket. As the matrix was most often still frozen during the collection, the matrix and bone material was easily held in place by the chisels.

Due to the weight limitations for removal by helicopter transport, the size and weight of the plaster jackets had to be restricted. Hanging load for a smaller Bell 212 helicopter is limited to 1200 kg, for the larger Super Puma it is about 2200kg, both were used in different field seasons. After turning the plaster jackets, the chisels were taken out, in order to reduce the jacket weight by gentle removal of excessive matrix by hand.

Larger skeletons had to be split in sections, and the jackets were separated by carefully removing and documenting the bones between them. After the specimens were transported to the laboratory at the Natural History museum in Oslo, they were left to thaw and dry for at least six months before preparation could be commenced. The same method for making the plaster jackets in the field is also used in the laboratory to flip between the different sides of the specimens.

Preparation and conservation

The total preparation time for each complete specimen has been experienced to lie somewhere between 800-2000 hours, depending on the size and preservation of the individual specimen. All the specimens were prepared mechanically and no acid preparation was used. Larger and/or fragile specimens were prepared directly in the plaster jackets, whereas some small or well-preserved specimens were removed element-by-element from the jacket for preparation. The tools used for the preparation of the Slottsmøya vertebrate fossils depended on the type of surrounding matrix and the preservation of the bone elements. For tough siderite- and gypsum-covered specimens; utility knives, dental tools and air scribes have been required. For cleaner and better-preserved material, removing the matrix with tweezers, cleaning with ethanol and then stabilising the elements with temporary adhesive is usually sufficient (see below). Other techniques, such as sandblasting with sodium bicarbonate, and in some cases iron powder, can be applied to fragile material after stabilising with fluid permanent adhesive. As in all fossil preparation (López-Polin 2012), several stages are involved in the preparation of the Slottsmøya Member marine reptiles, including A) initial cleaning, B) stabilisation and C) restoration.

Initial cleaning

As no consolidant is used in the field the cleaning process involves manual removal of the surrounding matrix and dust, and removal of secondary mineralisation such as gypsum (a calcium sulphate mineral, $CaSO_4{\cdot}2H_2O$) and siderite (an iron carbonate, $FeCO_3$) from the specimens. As the matrix is fragmented due to congelifraction, in most cases it was easy to remove excess matrix using smaller brushes and tweezers. After exposure of the bone surface, cotton buds dipped in 96% ethanol was found to be an efficient way of removing dust and brittle gypsum flakes from the fractured bone surface. This technique cannot be used on the specimens covered in large amounts of gypsum and siderite, as this material is often too strongly attached to the bone surface (Figure 4). However, the application of ethanol can help loosen bone-enveloping matrix for careful manual cleaning with scalpels. In an ichthyosaur specimen (PMO 222.669), the majority of the bone elements where covered in a thick layer of gypsum which could not be manually removed without damaging the bone surface (Figure 2B). In this instance, sandblasting using bicarbonate or iron powder removed most of the gypsum without damaging the bone surface. Tests of different sandblasting media were performed and bones were inspected by binoc-

Figure 3. The excavation process of Spitsbergen Jurassic-Cretaceous marine reptiles. A, The application of dampened toilet paper. B, The application of plaster-saturated burlap. C, The plaster is held in place during hardening. D, The plaster jackets are separated from the ground by chisels and rope is used to secure them. E, the plaster jacket after flipping. Photos courtesy of Erik Tunstad.

ulars before and after. An alternative gypsum dissolution method developed and described in detail in Druckenmiller *et al.* (2012), was to submerge bone elements in a sodium chloride solution for 1-3 days at 25°C. Druckenmiller *et al.* (2012) tested this method on an ichthyosaur paddle (PMO 214.578), and succeeded in removing gypsum crystals from the bone surface and in between fractures. However, this method cannot be used on highly fractured and fragile material, as the gypsum crystals in many cases participate in holding the fractured bone elements together.

One of the plesiosaur specimens (PMO 216.839) displayed a different preservation type to the other material: the bones were covered in gypsum, siderite, jarosite ($KFe^{3+}{}_3(SO_4)_2(OH)_6$), a hydrous sulphate with potassium and iron and pyrite (FeS_2), an iron sulphide. The vascular spaces inside some of the bone elements were filled by pyrite. Disintegration by pyrite decay is a major conservation issue and to limit the risk of future pyrite decay, this specimen had to be significantly cleaned prior to adhesive application and remains under close observation. As the material collected consists of several thousand bones no special storage with climatic control has been possible to finance.

In a plesiosaur specimen (PMO 222.663), large amounts of siderite were present in the surrounding matrix and on the bone elements, which required a combined approach of sandblasting using bicarbonate powder, and then applying air scribes and scalpels to reveal the bone surface. In most cases, this combined approach has proven to be the most efficient method to clean the Slottsmøya Member bone material.

Stabilisation

Following the initial cleaning process, the specimens require stabilisation. As most specimens have undergone significant congelifraction due to seasons of freezing/thawing, use of a reversible adhesive was required. The temporary adhesive used for stabilisation is a polyvinylacetate (PVAC) of the "Mowilith®" line (Celvolit in certain countries), here referred to as Mowilith. This vinyl acetate homopolymer is sometimes used during preparation in Germany (Lippmann 1986; Wadewitz 1976), but is otherwise to our knowledge rarely used for fossil preparation elsewhere in Europe. The polymer is most commonly dissolved quickly in a solution of acetone, but can also be dissolved in 96% ethanol over several days. This reduces the risk of detrimental effects to the user and eases application and handling. Viscous solutions are mixed 1:2 (Mowilith granules: ethanol) and additional ethanol can be added to the solution to achieve the required viscosity. A higher viscosity is used for surface stabilising and a lower viscosity solution for penetrating and stabilising deeper into the bone pore space. Mowilith can easily be removed from the bone surface by the application of or submersion in ethanol and is therefore an effective stabiliser of the fractured material from Spitsbergen. In larger, three-dimensionally preserved specimens where bones are overlapping such as in the plesiosaurs PMO 222.663 (*Colymbosaurus svalbardensis*) and PMO 224.248 (see Roberts *et al.* 2017), temporary and permanent adhesives (Paleobond and Geodur, see below) were used to avoid the three-dimensional elements from collapsing when removing the underlying matrix or when removing bone elements for reconstruction. In addition to functioning as a stabiliser, Mowilith can also be used in the final stages of preparation as a coating. Used as a coating, it has prevented additional fracturing and acts as a barrier to atmospheric contaminants.

Restoration

After an extended period of drying/hardening following the Mowilith application (minimum 24 hours), individual bone elements were stable enough to be moved or repositioned for the final restoration process. Gypsum and calcite mineralisation in fractures had to be removed and the broken edges cleaned completely to allow for the application of adhesive (Figure 5). Due to the extensive degree of fracturing, temporary adhesive solutions such as Paraloid B72 dissolved in acetone was tried and deemed insufficient as the glued fractures could not support any weight strain. As a result, a number of non-reversible adhesives are used to reconstruct the elements (see discussion below).

For gluing major fractures that need to be able to tolerate some weight strain, the preferred adhesive is Jurassic Gel, made by Paleobond®. This adhesive can also be used to fill internal missing fragments of material, and can be matted (e.g. to avoid reflection in photographs) by gently brushing acetone or gently sandblast with bicarbonate powder over the dried adhesive. Other more fluid permanent adhesives were applied in areas with micro-factures or in order to glue smaller fragments of bone: ethyl-cyanoacrylate "Geodur" ® (three types, viscous, medium and fluid). These are usually applied using a pipette for increased accuracy and to avoid excess amounts of adhesive. All these permanent adhesives require the use of a hardener (Loctite 7452 activator idh. No. 88224). A penetrating adhesive (Paleobond® Penetrant Stabilizer PB002-12), can be used on heav-

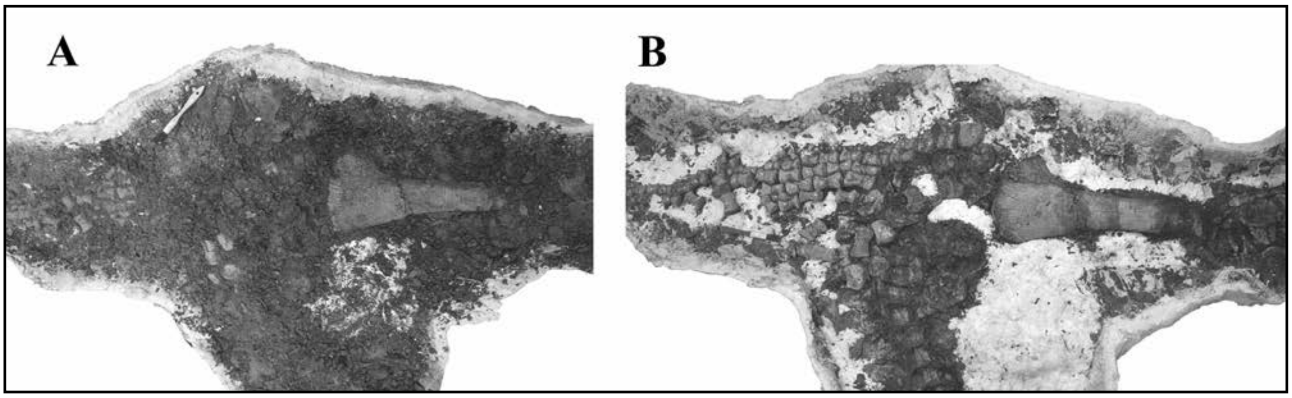

Figure 4: A plesiosaur hind limb and caudal vertebrae. A, before and B, after initial cleaning. The shale is heavily fragmented and easy to remove. The preparation time between the photos is 40 hours. Note the brush (~10cm) for scale.

ily weathered and micro-fractured bone elements and on tooth enamel. This adhesive successfully stabilised fragile and/or porous elements (e.g. ichthyosaur phalanges and teeth), and has so far stopped additional fracturing, rendering the specimen stabile enough for handling. This penetrating adhesive should be left to dry a minimum of 24 hours.

Some of the partially prepared specimens have been subject to additional deterioration over time by pyrite decay and/or secondarily formed gypsum crystals. One of these, the holotype of *Cryopterygius kristiansenae* (PMO 214.478, see Druckenmiller *et al.* 2012), was originally only prepared from one side and required further conservation of the opposite side. When the specimen was flipped, cleaning and stabilisation of this side was performed by removing the by-products of the decay. Areas which had been impregnated with Mowilith during the initial preparation, appeared to be in better condition than other areas. The removal of the sideritic matrix covering the bone elements and the application of Mowilith solution appears to have slowed down deterioration considerably. However, the specimen will require observation over time to see if these methods are sufficient for long-term preservation. A summary of the use of the different methods based on the general preservation types can be found in Table 1.

The use of computed tomography (CT) prior to complete preparation

For the past 40 years, computed tomography (CT) has been used to obtain three-dimensional information on fossil specimens (Conroy and Vannier 1984, Jungers and Minns 1979). Significant improvements to CT scanning technology and computer visualisation has made CT work easier, faster and at a higher resolution (Cnudde and Boone 2013, Sutton *et al.* 2014, Sutton 2008). Virtual preparation is a technique that can be used on fragile specimens, or where the matrix is hard to visually differentiate from the bone, as long as there is a density difference between

	Preservation type			
Method	*Siderite surrounding specimen*	*Gypsum flakes on surface*	*Gypsum and compact shale*	*Fracturing*
Manual cleaning with tweezers	x	x	x	x
Sandblasting with bicarbonate	x	x	x	
Ethanol clean using cotton buds		x		x
Application of Mowilith for stabilisation	after matrix removal	after matrix removal	after matrix removal	x
Manual preparation using air scribes and scalpels	x	only if necessary	x	
Use of penetrating permanent adhesive	after cleaning and matrix removal	after cleaning and matrix removal	after cleaning and matrix removal	x
Use of thicker permanent adhesives	after cleaning and matrix removal	after cleaning and matrix removal	after cleaning and matrix removal	for larger factures
Application of Mowilith for conservation	x	x	x	x

Table 1. A general summary of the methods used for the individual preservation types.

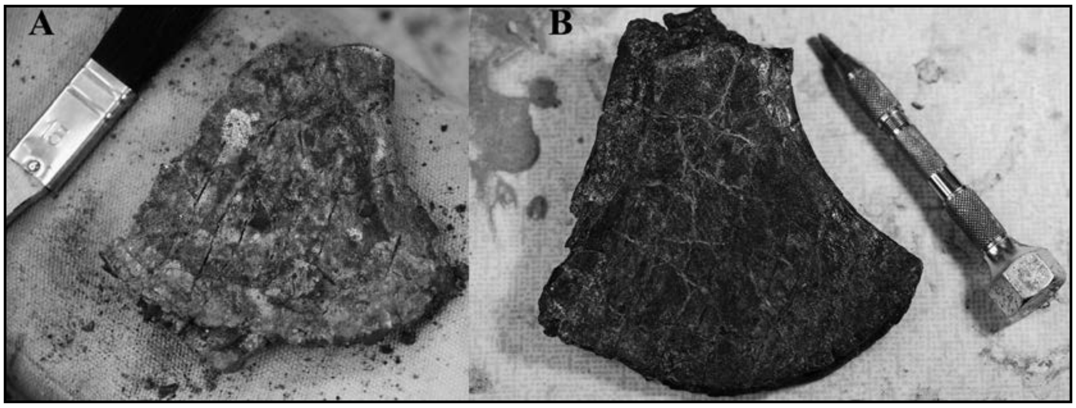

Figure 5: Clavicle of* Djupedalia engeri *(PMO 216.839). A, before cleaning, stabilisation and restoration; B, result after the completed preparation.

the bone material and the matrix. As shown by Larkin *et al.* (2010), CT or X-ray radiography can be a useful method to determine boundaries during the preparation of marine reptiles. In some cases, particularly in the preparation of cranial material, where bone elements can be extremely thin and often over/underlap each other, CT scanning can be used to interpret the extent of bone material and underlying bone elements.

For the fragile cranium of PMO 224.248, a cryptoclidid plesiosaur from Svalbard; µCT scanning was performed before and after complete preparation. The scanner used on the material was a Nikon XT H 225 ST at the Natural History Museum, University of Oslo, Norway. In some areas of the cranium of PMO 224.248, the matrix was particularly hard and firmly attached to the bone, resulting in damage during early preparation. Due to this issue, the decision to scan prior to any further preparation was made.

The CT machine's ability to penetrate fossil specimens depends on the density, thickness and mineralisation of the specimen, as well as the contrast to the surrounding matrix (Cnudde and Boone 2013). Therefore, the individual preservation of any specimen must be taken into account when using filters and determining beam energy and voltage. A major limitation of CT scanning is usually the size of the specimen itself, as few scanners can accommodate large specimens and even then, objects often have to be scanned in sections (e.g. Larkin *et al.* 2010). The cranium of PMO 224.248, was scanned in three sections due to the limited range of view in the scanner (10x10cm). The scans were later meshed together during post-processing in Avizio to form a single high-resolution scan. Images were then later processed using ImageJ.

Due to the size-issue, the cranium had to be positioned snout-up in the µCT scanner in a secured cradle. Trials were completed using two different types of cradles: the first cradle made from plaster and the second using a dense foam material (Ethafoam). Although the resulting µCT images for the plaster cradle were sufficient to utilise the images as a basic visual aid in manual preparation, the plaster cradle caused a loss of resolution as the dense material was harder to penetrate by the X-rays and some of the bone material displayed a similar density to the plaster. This consequently required the additional effort of segmenting out the plaster cradle during the post-processing. Following this attempt, Ethafoam was cut to fit the cranium and lined with a thin mat of cotton wool covered by plastic foil (Figure 6). This cradle method secured the specimen and reduced the post-processing time significantly, due to the lightweight and low-density support material.

The manual preparation of the cranium of PMO 224.248 was performed using µCT images as a reference, allowing for safe matrix removal without causing damage to underlying bone elements (Figure 7). Areas such as the palate, alveoli, basicranium and external naris could be prepared in more detail using this method. The technique was crucial to avoiding damage to the thin bone walls of the alveoli and the palate, which were barely visible using a hand lens (Figure 8). As the posterior section of the cranium

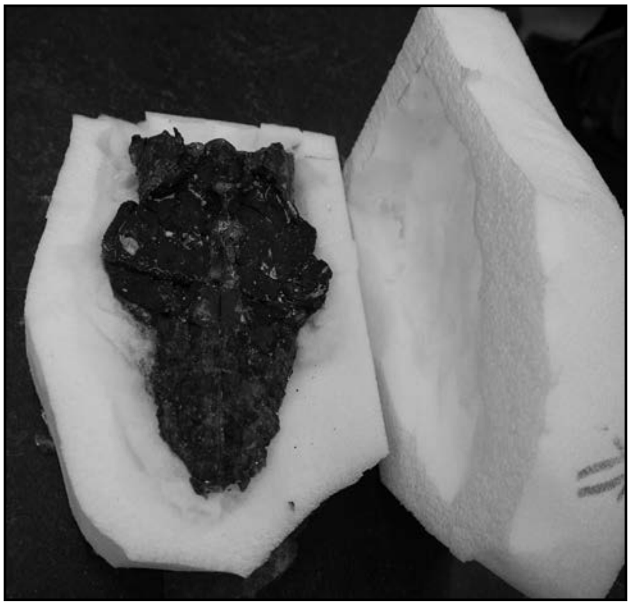

Figure 6: The skull of a cryptoclidid plesiosaur PMO 224.248 in the Ethafoam cradle used for the µCT scan. The skull is 22.5 cm in total length.

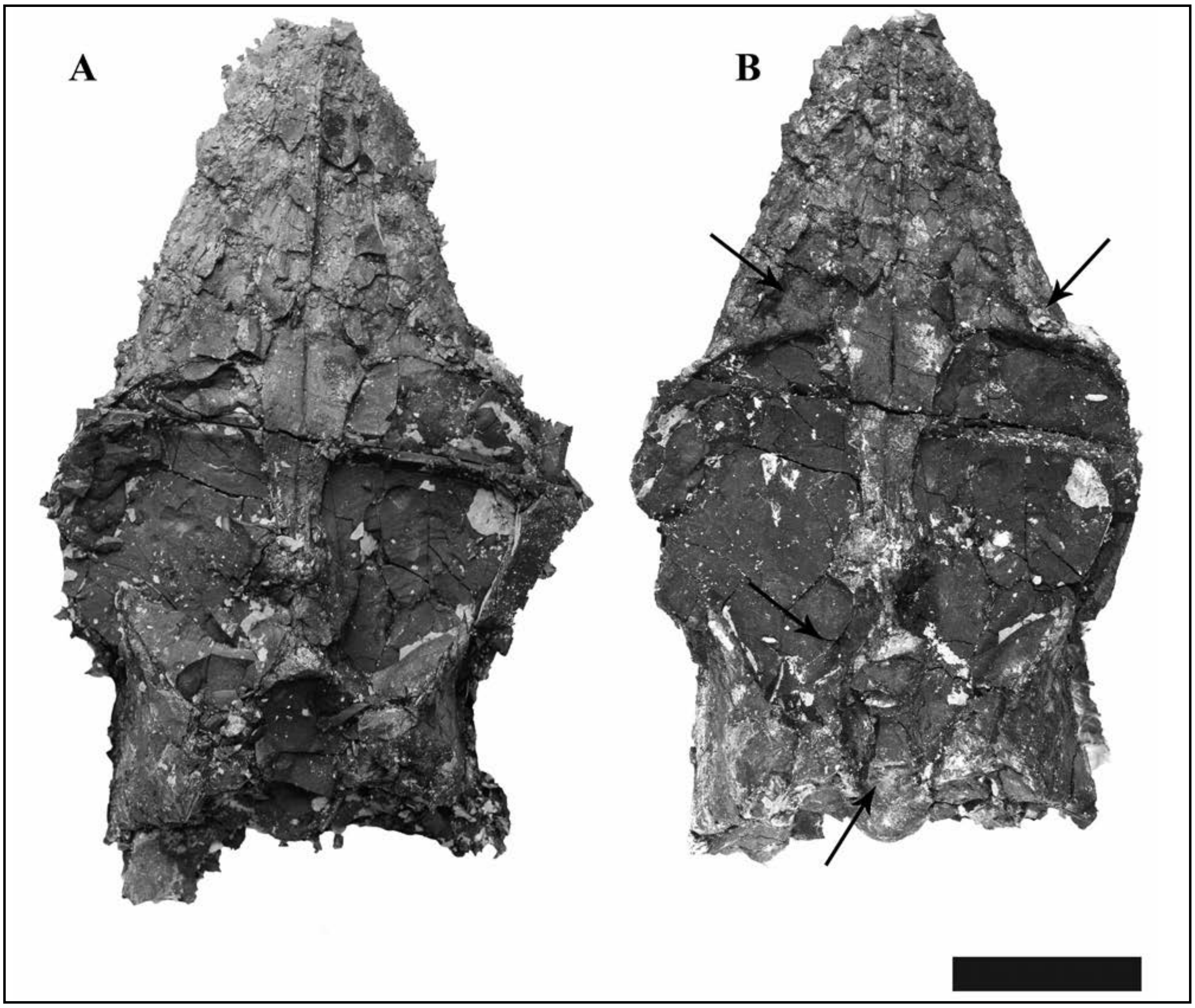

Figure 7. The cranium of a cryptoclidid plesiosaur PMO 224.248 in dorsal view. A, before and B, after computed tomography was used to assist the final preparation. The arrows indicate regions where the CT scans where used as a "guide" to identify the bone element depth. Scale equals 5 cm.

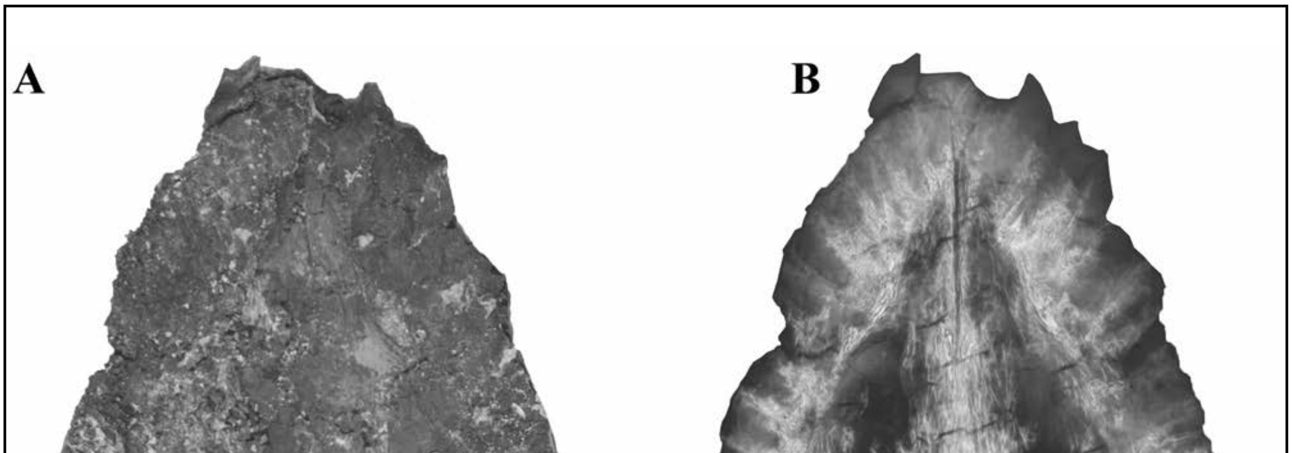

Figure 8: The prepared snout of PMO 224.248 in ventral view. A, a photograph; B, the µCT scan of the same area. Note the light-coloured barite and/or calcite filling the vascular canals in the bone. Scale bar equals 2cm.

was generally uncompressed, the removal of matrix in certain areas could potentially cause the elements to collapse on themselves. To avoid this, a virtual preparation of the braincase was completed using Avizo Fire (FEI Company, V.8). The resulting three-dimensional model included most of the necessary taxonomic information deeming further manual preparation an unnecessary risk.

Discussion

The reversible adhesives used for conservation and stabilisation processes in the laboratory are most commonly vinyl (e.g. Mowilith) or acrylic (e.g. Paraloid B72) consolidants. The temporary adhesives Mowilith and Paraloid B72 are both stable and are to a degree reversible; however Paraloid B72 is more frequently used and has a long history of use in museums outside Germany (e.g. Carpenter and Radley 2010, Padilla *et al.* 2010, Sassoon *et al.* 2010). Similar to Paraloid B72, Mowilith has documented advantages and disadvantages and in the literature, is often seen to perform equally to Paraloid B72. Mowilith has been shown not to influence oxygen isotope analysis, if removed prior to sampling (Stephan 2000). However, similar substances have been shown to influence 14C analysis (Law *et al.* 1991). Another study testing multiple reversible adhesives dissolved in acetone (Paraloid B72, Primal AC61 and Mowilith) showed that these can distort surface traits when using an optical or electron microscope (Fernández-Jalvo and Monfort 2008). Consolidants are often over used in fossil preparation and should be applied minimally. Some material, however, including highly fractured materials such as ours have no option but to be consolidated (see e.g. Larkin 2010). For the plesiosaur cranium PMO 224.248, we found no visible artefacts from the application of Mowilith using computed tomography, suggesting the distortions are only visible on the surface. Based on our observations, Mowilith has been more successful in stabilising highly fractured material such as is shown in Figure 2. Unlike Paraloid B72, Mowilith can be easily mixed with ethanol rather than acetone, making the solution less harmful to the technicians' health. In addition, similar to the use of Paraloid B72, the use of Mowilith has also restricted the detrimental effects from atmospheric changes (e.g. pyrite decay) affecting the prepared specimens over the past decade (Larkin *et al.* 2010). The prepared specimens will remain under close observation to see if the stabilising effect of the Mowilith deteriorates in the future.

The use of cynoacryoloids as permanent adhesives on fossil material has been debated. This is predominantly due to the near irreversibility of the substances and the unknown strength duration of the individual types, as they have not been subject to long historical use (Shelton and Chaney 1994). Temporary adhesives are usually more pliable and are unsuitable for bearing the weight strain in significantly fractured, three-dimensional material. For some of the Slottsmøya Member specimens, the use of cynoacryoloids was therefore deemed necessary in order to be able to study and move the specimens without risking causing permanent damage. If avoidable, we recommend not to use these substances due to their almost irreversible nature. However, for highly fractured elements that are required to bear weight strain and remain stable, they are indispensable.

While vertebrate palaeontologists frequently use CT methods and radiography to interpret internal and hidden bone structures, there are also multiple advantages of using CT to virtually prepare specimens. These include the reduction of potential damage to fragile and thin bone elements by over-preparation and also being able to visualise the extent and depth of the individual bone elements. In our experience, the µCT images have proven central not only to the taxonomic description of the internal cranial anatomy of PMO 224.248; it has avoided the need for manual preparation of certain areas altogether. In addition, the CT images have also helped in further understanding the topology of the palate and braincase of the specimen during the manual preparation. In these regions, the bone material is often extremely thin and fragile and utilising CT images served as a guide to judge the margins of the individual elements. A problematic issue with CT scanning on partially or completely compressed material is that images in the cross sectional dimension often have numerous artefacts and are not as clear as other dimensions. This is because the scanner has to penetrate a thicker section of bone and/or matrix. Some of these artefacts (e.g. ring artefacts) can be reduced or removed during post-processing, or can minimised by utilising different filters. The continually improved resolution of computed tomography can be used to avoid destructive sampling, over-preparation and for describing microanatomy in fossil material (Sutton *et al.* 2014, Takeda *et al.* 2016).

We hope that this report on the marine reptiles from the Slottsmøya Lagerstätte will provide a reference for other researchers wanting to excavate and work on fossil vertebrate material from high-latitude regions.

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COMPARING SULPHAMIC ACID TO ACETIC AND FORMIC ACIDS FOR THE PREPARATION OF LARGE MESOZOIC MARINE REPTILE FOSSILS, AND A METHOD FOR MONITORING RESIDUAL ACID AND SALT REMOVAL FOLLOWING ACID PREPARATION

by Leslie F. Noè, Marcela Gómez-Pérez, Santiago Padilla-Bernal

Noè, L.F., Gómez-Pérez, M., Padilla-Bernal, S. 2019. Comparing sulphamic acid to acetic and formic acids for the preparation of large mesozoic marine reptile fossils, and a method for monitoring residual acid and salt removal following acid preparation *The Geological Curator* 11 (1): 81-92.

Chemical preparation is an important technique in palaeontology that uses a dilute aqueous acid solution to remove calcareous matrix from fossils, but which leads to the evolution of salts as a by-product. Acid preparation is usually undertaken using formic and acetic acids, whereas sulphamic acid has only rarely been considered. Sulphamic acid is a strong acid, with many industrial uses, but which has fewer health and safety concerns, and produces fewer irritant fumes, than formic or acetic acids. Three comparative procedures were undertaken to understand the action of sulphamic acid in relation to formic and acetic acids, using calcareous matrix from Colombian (South American) large Mesozoic marine reptiles. The results of these procedures indicate sulphamic acid acts in a comparable manner to formic acid, and more rapidly than acetic acid, in terms of rate of matrix removal. A fourth procedure investigated the removal of acid and salt residues following sulphamic acid preparation of a Colombian large Mesozoic marine reptile fossil, a process essential for the long-term survival of any acid prepared specimen. The fossil was immersed in type 1 deionized water, and increasing electrical conductivity was used as a proxy for ionic leaching. The results imply the preparators 'rule of thumb' of soaking a specimen in water for three times the length of time spent in the acid solution, is inadequate to ensure satisfactory removal of acid and salt residues. Although tested on a specimen prepared using sulphamic acid, the technique for post-preparation ion removal is equally be applicable to all fossils prepared using sulphamic, formic or acetic acids in aqueous solution.

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Introduction

Acid preparation is a well-established chemical technique used in palaeontology to liberate fossils from a calcareous matrix (Rixon 1976; Lindsay 1987; Blum *et al.* 1989), and this article expands on the use of sulphamic acid (Padilla and Parra 2009; Padilla *et al.* 2010). Chemical preparation has the advantage over standard mechanical techniques that it is able to remove enclosing lime-rich rock matrix, molecule-by-molecule, whilst leaving the enclosed fossils relatively unharmed thereby yielding exquisitely prepared fossils (Rudner 1972; Evander 1996a; McCrae and Potze 2007). However, acid preparation may lead to specimens that are relatively more brittle and therefore fragile than mechanically prepared specimens. Acid preparation works because in aqueous solution hydronium ions (H_3O^+) attack the calcareous matrix by combining H^+ ions with $CaCO_3$ (or other carbonate), releasing carbon dioxide gas (CO_2) and calcium cations (Ca^{2+}) into solution (Lindsay 1987; Hellawell and Nicholas 2012), and produces dissolved calcium salts (Lindsay 1987). The precise nature of the calcium salt produced, depends upon the acid used, for example, acetic acid yields calcium acetate ($Ca(H3CCOO)_2$), and formic acid generates

Acid name	Chemical Formula	State	Acidity pK_a	Salt liberated	NFPA 704 rating			Notes
					H	F	R	
Sulphamic	NH_2SO_3H (monoprotic)	S	1.18	Sulfamate	3	0	0	Odorless, dust irritant to eyes and skin
Formic	HCOOH (monoprotic)	L	3.74	Formate	3	2	0	Highly pungent, corrosive to and readily absorbed by the skin
Acetic	CH_3COOH (monoprotic)	L	4.77	Acetate	3	2	1	Pungent, corrosive to skin, mixing with water liberates heat

Table 1. Some comparative data on sulphamic, formic and acetic acids.
Formic and acetic acids are most commonly used for the chemical preparation of fossils, and the use of sulphamic acid is described here; all three are weak (incompletely disassociated) acids. A monoprotic acid donates one H^+ ion per molecule in aqueous solution; pKa is the acid dissociation constant at 25ºC, the lower the number the stronger the acid; NFPA 704 ratings are a US hazard warning scheme (see text for details). Use of all acids is potentially dangerous and should be undertaken by competent staff wearing suitable personal protective equipment and having completed the required risk and hazard assessments; concentrated acids must always be added to water to produce an aqueous solution, and users should consult local and national regulations and manufactures material data safety sheets (MSDA) regarding safe use of acids in the laboratory. Abbreviations: F, Flammability; H, Health; L, Liquid; R, Reactivity; S, Solid. Data from NFPA. 2007; Metzger 2012; Le Berre 2013; Hietala 2016.

calcium formate ($Ca(HCOO)_2$) (Le Berre 2013; Hietala 2016).

Acid preparation of fossils typically uses a dilute (3-15%; although usually the lower end of this range) acid solution, most commonly formic (HCOOH) or acetic (CH_3COOH) acids (Whybrow 1985; Blum *et al.* 1989). Following a short, unprotected immersion in acid for surface cleaning (Stringer et al. 1985), chemical preparation is a cyclic, multi-step process consisting of: protecting exposed bone using an acid resistant consolidant; immersion of the protected specimen in acid for a period of hours; washing and cleaning the specimen to remove excess acid, liberated salts and loosened matrix; drying; and application of additional layers of acid resistant consolidant to protect newly exposed bone (Lindsay 1987; Whybrow and Lindsay 1990). An additional phase of mechanical preparation can be undertaken, prior to application of the consolidant, to speed up removal of acid resistant matrix or to reduce the number of acid immersion cycles (Rutzky *et al.* 1994).

Acid preparation of fossils was originally undertaken using hydrochloric and hydrofluoric acids (Holm 1890; Walton 1923; Lang 1926; Bulman 1931), which are inorganic (or mineral) acids. However, mineral acids are highly aggressive and have been gradually replaced by weaker organic acids, such as acetic and formic acids (Toombs 1948; Toombs and Rixon 1950; Whybrow 1985; Rixon 1976; Lindsay 1987; Brown 2013). Organic acids are weak because they dissociate incompletely, whereas mineral acids are strong because they dissociate almost completely in water (>99.9%) (Atkins and Jones 1999). The strength of an acid can be quantitatively gauged from its acidity constant (Ka); and relative strengths for weak acids are compared by the negative logarithmic dissociation constant, pKa (-log10 Ka), where a larger value indicates less dissociation, and a hence weaker acid (Evander 1996a).

Sulphamic acid (amido-sulfuric acid, Metzger 2012, sulfamic acid in American English) has been widely used to remove calcareous ($CaCO_3$-rich) limescale deposits from household, marine and industrial equipment (Moerman, *et al.* 2014), but has only rarely been used for chemical preparation of fossils (Padilla *et al.* 2010; Griffin and Nesbitt 2016). In industry, sulphamic acid has been shown to have little effect on underlying substrates, usually metal and plastic pipes or containers, few health and safety concerns and less need for fume extraction (Moerman, *et al.* 2014). Hence sulphamic acid should be both applicable and beneficial for the removal of calcareous matrix from fossils (Table 1), although corrosion of metal may occur, so use of plastic implements and pipework is highly recommended. Sulphamic acid is sold as a crystalline powder that is stable, non-volatile, non-hygroscopic (does not readily absorb atmospheric water vapor) with a melting point of 205°C (Metzger 2012). Hence, with suitable personal protective equipment, the pure acid can be handled with a powder scoop, allowing for relatively safe in-laboratory weighing on a balance, and movement to a water bath in a plastic receptacle, thereby minimizing the spill risks associated with a concentrated liquid acid, such as glacial acetic or formic acids. Sulphamic acid does not produce hazardous fumes when added to the water (Metzger 2012), unlike formic and acetic acids (Le Berre 2013; Hietala 2016), and preparation with sulphamic acid releases only CO_2 gas, so ventilation requirements are minimal. Sulphamic acid yields calcium sulfamate salts ($CaH_4N_2S_2O_6$) in solution.

One particular problem with acid preparation, is that without adequate post-preparation rinsing, residual acids and evolved salts can cause damage during preparation, subsequent storage or display of specimens, and these effects might only be apparent long after preparation has been completed (Rixon 1976; Jeppsson *et al.* 1985; Lindsay 1987; Rutzky *et al.* 1994). Salts resulting from acid preparation crystallize, which on the surface causes unsightly 'blooms' and internally cause volumetric changes, both of which can cause irreparable harm the prepared specimen (Stringer *et al.* 1985; McCrae and Potze 2007). Both acid and salt residues can result in permanent damage, with associated information loss, or ultimately result in complete destruction of a fossil specimen. For this reason, it is essential to leach an acid prepared specimen as fully as possible of residual acid and salt by-products, and a preparators ´rule-of-thumb' of leaving a specimen in running water for approximately three (two to four) times the length of time the specimen has been immersed in acid, has been generally applied (e.g. Rixon 1976; Stringer *et al.* 1985; Lindsay 1987).

Aims-The aim of this paper is to assess the suitability of sulphamic acid for chemical preparation of large vertebrate fossils and compare it to the commonly used formic and acetic acids. We also propose a method to determine the time required for adequate removal of residual acid and soluble salts following sulphamic acid preparation, a technique which can be applied to all fossil specimens prepared aqueous acid solution, irrespective of the acid used.

Institutional Abbreviations-CIP, Centro de Investigaciones Paleontológicas, km 4 vía Santa Sofia, Vereda Monquirá, Villa de Leyva, Boyacá, Colombia (specimen numbers CIP-CBP followed by a number); MJACM, Museo El Fósil, Vereda Monquirá, Boyacá, Colombia.

Materials and methods

Specimens

All specimens referred to here reside in the Centro de Investigaciones Paleontológicas (CIP, km 4 vía Santa Sofia, Vereda Monquirá, Villa de Leyva, Boyacá, Colombia) and have specimen numbers CIP-CBP followed by a number. Matrix samples from four specimens of large Colombian Mesozoic marine reptiles were utilized for four procedures: CIP-CBP4 (a pliosaurid); CIP-CBP16 (a partial ichthyosaur cranium); CIP-CBP17 (an ichthyosaur); and CIP-CBP21 (a pliosaurid). CIP-CBP21 was specifically chosen because of extensive ferric (Fe^{3+}) iron in the matrix; the matrix of the remaining specimens contained minimal ferric iron.

Chemicals and equipment

Sulphamic acid, of United States Pharmacopeia (USP) grade, was sourced under the trade name DESCALEX, which incorporates a pH indicator; Paraloid B72 (Acryloid within the USA) an ethyl methacrylate copolymer (Chiantore and Lazzari 2001), was used as an acid resistant consolidant; industrial grade ethanol (96%, denatured) was used to dissolve the Paraloid B72 (ethanol can be replaced by acetone where regulations allow), and to displace water following acid preparation. Mass (to the nearest gram) and pH (to the nearest complete unit) were taken using a standard laboratory balance and pH meter. The electrical conductivity of the water bath for procedure P4 was monitored using a Hannah Instruments HI 98308 Pure Water Tester (range: 0.0-99.9 µS/cm; resolution 0.1µS/cm; accuracy ± 2% full scale at 20ºC with automatic temperature compensation).

Acid preparation method

Sulphamic acid at 4% weight to volume (w:v) was used for an initial immersion of CIP-CBP16, used in procedure P4, which was then prepared, according to CIP protocols (Padilla *et al.* 2010). When much matrix was present 4% w:v Sulphamic acid was used, and a reduced concentration of 2% w:v was used for subsequent acid immersions because more fossil bone was exposed. All acid solutions were saturated with calcium phosphate, $Ca(PO_4H_2)_2$, to inhibit chemical action on the phosphate compounds in the exposed bone (Lindsay 1987; Rutzky *et al.* 1994). Acid immersion times were three to five hours. Between acid bath immersions, the specimen was rinsed under running water for at least one hour and subsequently immersed in a tank of still water for approximately 12-14 hours. The specimen was allowed to air dry for one to two days (depending on ambient relative humidity), after which it was immersed in ethanol to displace residual moisture, and dried. Exposed bone was coated with multiple layers of Paraloid B72 in ethanol (5% to 15% w:v), in gradually increasing concentrations, as an acid-resistant consolidant (Evander 1996b; Davidson and Alderson 2009). Newly exposed cracks and crevices were injected with 5% w:v Paraloid B72 dissolved in ethanol, and where necessary filled with dental wax or 'Plasticine'-type modelling clay to prevent acid penetration. The specimen was re-immersed in acid

	CIP-CBP4			CIP-CBP17			CIP-CBP21		
	S	F	A	S	F	A	S	F	A
Cycle	**Mass (g), pH**								
0	10, 1	10, 2	10, 2	10, 1	10, 2	10, 2	10, 2	10, 2	10, 2
1	7,1	6, 3	8, 3	7, 1	6, 3	9, 3	9, 1	10, 2	9, 2
2	4, 1	4, 4	5, 4	4, 1	3, 3	7, 4	9, 1	9, 2	8, 2
3	1, 1	1, 4	4, 4	1, 1	1, 3	5, 4	8, 1	8, 2	8, 2
4	0, 2	0, 4	3, 4	0, 1	0, 3	3, 4	8, 1	8, 2	8, 2
5	-	-	1, 4	-	-	2, 4	7, 1	7, 2	7, 2
6	-	-	0, 4	-	-	1, 4	7, 1	7, 2	7, 2
7	-	-	-	-	-	0, x	6, 1	7, 3	7, 3

Table 2. Comparative dissolving power of acetic, formic and sulphamic acid on single blocks of calcareous matrix over multiple acid immersion cycles (procedure P1).
Results from the dissolution of 10g blocks of untreated matrix from three different vertebrate specimens (CIP-CBP4, a pliosaurid; CIP-CBP17, an ichthyosaur; CIP-CBP21, a pliosaurid), each in 100ml of 2% weight: volume aqueous solution of three different acids (acetic, formic and sulphamic) in repeated two hour immersion cycles (procedure P1). Cycle 0 represents the starting data, and subsequent rows indicate the matrix mass (in grams) and pH at the end of the acid bath cycles, with the two values separated by a comma; a pH of 2 or 3 indicates active acid remains. Acid action ceased on specimen CIP-CBP21 due to the presence of unreactive ferric iron minerals in the matrix inhibiting acid access to the carbonate. Abbreviations: A, acetic acid; F, formic acid; S, sulphamic acid; CIP-CBP, specimen numbers from which the matrix samples were removed; x, data not recorded.

and the cycle repeated until sufficient matrix was removed. Following completion of acid preparation, normal final rinsing was undertaken under running water for at least three times the length of the final acid immersion, after which the specimen was allowed to air dry and excess consolidant removed using ethanol. Although temperature was not controlled for, each of the procedures were undertaken at ambient (normal laboratory) temperatures.

Procedures

Procedure P1 tested matrix dissolution and acid consumption using single 10g (dry weight) matrix blocks from each of three specimens (CIP-CBP4, 17, 21). Each block was immersed in 100ml of 2% w:v aqueous solutions of sulphamic, acetic or formic acid. After two hours acid immersion, the pH of the residual acid was recorded, and any remaining matrix washed, dried and weighed. The procedure was repeated in fresh acid solution until the matrix blocks were completely dissolved.

Procedure P2 explored surface area, matrix dissolution and acid consumption using the same protocol as for procedure P1, except the 10g matrix blocks were broken into several smaller fragments to increase the surface area. After two hours immersion, the pH of the residual acid, and the dry weight of any remaining matrix fragments were recorded.

Procedure P3 examined matrix dissolution and acid consumption for longer immersion times using triplicate samples of different weight, unbroken matrix blocks from CIP-CBP4, and each subjected to a single eight-hour acid bath in 500ml of 2% w:v aqueous solutions of sulphamic, acetic or formic acid. The pH of the acid and the dry weight of the matrix were recorded before and after the acid bath cycle to determine how much acid was spent in relation to the mass of matrix removed.

Procedure P4 assessed residual acid and salt removal following standard sulphamic acid preparation for CIP-CBP16. Following acid preparation and standard rinsing, CIP-CBP16 had a dry weight of 7.1kg and an approximate volume of 3 litres (determined by Archimedean water displacement). The specimen was then immersed in type 1 deionized water, defined as water with an electrical resistivity greater than 10 megohms/cm (MO/cm), or an electrical conductivity of less than 0.1 microsiemens/cm (µS/cm) at 25°C (ASTM 2018). Electrical conductivity of the water bath was monitored over an 11-week period, with measurements taken on 40 working days over a 75-day period.

Results

Procedure P1

Sulphamic and formic acids required four two-hour cycles to entirely dissolve 10g of matrix from CIP-CBP4 and CIP-CBP17, whereas acetic acid required six or seven cycles to achieve the same result (Table 2). Throughout the process, the sulphamic acid (except for in a single instance with matrix from CIP-CBP4) remained at its starting pH of 1, whereas the pH of the formic and acetic acids increased to pH 3, or more commonly pH 4, after each two-hour acid cycle. The matrix from CIP-CBP21 dissolved more slowly in all three acids and showed little evidence for total dissolution even after seven acid immersion cycles. In all cases with CIP-CBP21, the pH of the acids did not change, in contrast to the acid acting on the matrix from the other two specimens.

Procedure P2

When the 10g masses of matrix were broken into smaller pieces, producing a larger surface area, the number of acid bath cycles required to entirely dissolve the matrix remained essentially the same as in procedure P1 for sulphamic and formic acids (around four acid bath cycles each), whereas the number of cycles was slightly reduced to six (from seven) for acetic acid (Table 3). However, in all three acids, the initial rate of dissolution was much enhanced, with only 1-3g of matrix remaining after the first acid immersion cycle in sulphamic and formic acids, compared to the 6-7g in procedure P1. The pH of the sulphamic acid generally increased more than in procedure P1, but less than with formic or acetic acids. In all three acids, the ferric iron-rich matrix associated with CIP-CBP21 dissolved much more slowly than the matrix from the other two specimens, but somewhat more rapidly than in procedure P1. As with procedure P1, the increase in pH for the acid containing matrix from CIP-CBP21 was much less than for the other two matrix samples.

Procedure P3

Longer acid bath treatments with larger masses of matrix show that, on average, sulphamic acid removed 4.4g over an eight-hour period, with an associated decrease in acidity from pH 1 to pH 2 (Table 4). Formic acid removed an average of over 7.45g and acetic acid 2.6g of matrix respectively under the same conditions, and both of these acids showed a greater decrease in acidity from pH 2 to pH 4.

Procedure P4

The post preparation leaching experiment on CIP-CBP16 showed a gradual increase in the ionic concentration of the type 1 deionized water from 0 to 380µS/cm over the 11-week trial period (Fig 1). During this time, the rate of increase in electrical conductivity gradually reduced, and reached a plateau of less than 1% increase by the termination of the procedure.

Discussion

Prior to preparation, large vertebrate fossils often exceed several hundred kilograms in weight, and when encased in a lime-rich matrix the use of chemical preparation is one of the most effective methods of matrix removal. In the Villa de Leyva region of central Colombia, vertebrate fossils from the Paja Formation Lagerstätte (Noè and Gómez-Pérez. 2019 in press) are often preserved in large calcareous concretions, some with a high ferric iron content, and sulphamic acid has been used for their preparation (Padilla *et al.* 2010). The procedures reported here were designed to test the efficacy of sulphamic acid, compared to acetic and formic acids, for the preparation of large fossil vertebrates, and to monitor the time required for leaching of acid and soluble salt residues following acid preparation.

Efficacy of sulphamic acid

Procedures P1 and P2 indicate that over a series of two-hour acid bath cycles, sulphamic acid exhibits a comparable level of matrix removal to formic acid, both in terms of rate and volume, whilst the weaker acetic acid requires approximately 50% more acid immersion cycles for the same result. The relative lack of action by all three acids on the matrix of CIP-CBP21 confirmed that ferric iron will eventually render matrix unreactive to acid without additional mechanical preparation, or treatment by the Waller Method or thioglycolic acid (Howie 1974; Rixon 1976; Blum *et al.* 1989). Procedure P2 indicates that greater matrix surface area increases acid reaction, although this does not always reduce the number of acid immersion cycles required for complete dissolution of the matrix fragments. In this respect, sulphamic acid is as effective as formic acid, and acts more rapidly than acetic acid. However, procedures P1 and P2 also indicate that the rate of decrease in acidity (increase in pH) for sulphamic acid is less than for formic and acetic acids. Hence, sulphamic acid remains closer to its original pH 1, whereas the pH of both formic and acetic acids increased to pH 3-4 from an original pH 2. This represents a one to two order of magnitude reduction of hydronium ion concentration in the formic and acetic acids. This result means the sulphamic acid solution can be re-used for short acid preparation cycles, requiring less frequent replenishment than when using formic or acetic acids.

The results of the comparative performances of sulphamic, formic and acetic acids during longer acid preparation cycles of procedure P3 were somewhat unexpected. Sulphamic acid, as a stronger acid (Padilla *et al.* 2010; Metzger 2012), had been expected to remove a larger amount of matrix than either formic or acetic acids, but procedure P3 placed sulphamic acid between formic and acetic acids in terms of mass of matrix removed. However, the lower pH change of sulphamic acid over the eight-hour cycle is consistent with both the lower mass of matrix removal, and a lower pKa, compared to formic acid (Table 1). Nevertheless, sulphamic acid seems to work for longer acid bath cycles without such

Cycle	CIP-CBP4			CIP-CBP16			CIP-CBP21		
	S	F	A	S	F	A	S	F	A
	Mass (g), pH								
0	10, 1	10, 2	10, 2	10, 1	10, 2	10, 2	10, 2	10, 2	10, 2
1	3, 1	3, 3	7, 3	2, 1	1, 3	4, 3	8, 1	8, 2	9, 2
2	2, 1	2, 3	5, 4	1, 1	1, 4	2, 4	8, 1	8, 2	9, 3
3	2, 2	1, 3	4, 4	1, 2	0, 4	2, 4	7, 1	8, 2	8, 3
4	1, 2	0, 4	2, 4	0, 2	-	1, 4	7, 1	7, 3	8, 4
5	0, 2	-	1, 5	-	-	0, 5	6, 1	7, 3	7, 4
6	-	-	0, 4	-	-	-	-	-	-

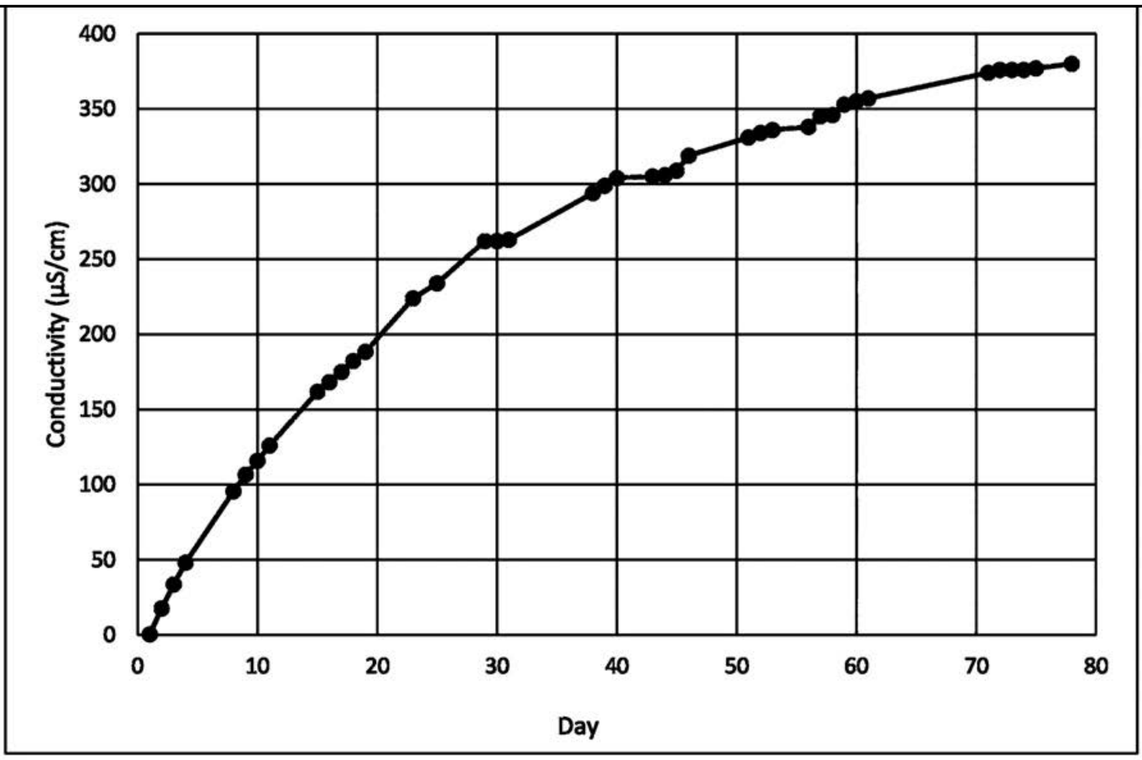
Table 3. Comparative dissolving power of acetic, formic and sulphamic acid on broken blocks of calcareous matrix over multiple acid immersion cycles (procedure P2).
Results from the dissolution of 10g blocks of untreated matrix broken into fragments from three different vertebrate specimens, each in 100ml of 2% weight: volume aqueous solution of three different acids (acetic, formic and sulphamic) in repeated two hour immersion cycles (procedure P2). Cycle 0 represents the starting data, and subsequent rows indicate the matrix mass (in grams) and pH at the end of the acid bath cycles, with the two values separated by a comma; a pH of 2 or 3 indicates active acid remains. Acid action ceased on CIP-CBP21 due to the presence of unreactive ferric iron minerals in the matrix inhibiting acid access to the carbonate. Abbreviations: A, acetic acid; F, formic acid; S, sulphamic acid; CIP-CBP, specimen numbers from which the matrix samples were removed.

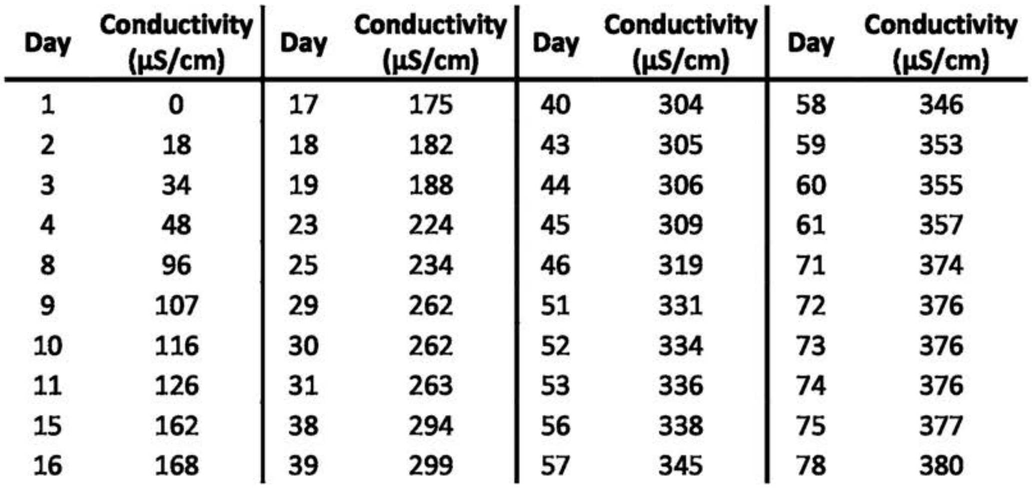
aggressive action as formic acid, which removed twice as much matrix, and four times as much matrix as acetic acid, over the same eight-hour cycle. However, the formic acid showed a greater increase in pH, equivalent to a hundredfold consumption of hydronium ions, in association with the greater matrix removal. Sulphamic acid is a stronger acid than formic acid, so the slower rate of activity of sulphamic acid may be due to the detailed chemistry of the acids. However, the results of procedure P3 are difficult to interpret, because they are confounded by differences in original matrix mass, surface area, and matrix heterogeneity between samples (Padilla *et al.* 2010).

Sample no.	Mass (g)			pH	
	Initial	Final	% Loss	Initial	Final
Sulphamic acid					
1	37.0	32.5	12.2	1	2
2	25.7	21.4	16.7	1	2
3	19.0	14.6	23.2	1	2
Formic acid					
4	33.3	25.5	23.4	2	4
5	25.9	18.5	28.6	2	4
6	21.4	14.2	33.6	2	4
Acetic acid					
7	24.5	21.6	11.8	2	4
8	18.0	15.7	12.8	2	4
9	14.1	11.4	19.1	2	4

Table 4. Comparative dissolving power of acetic, formic and sulphamic acid on single blocks of calcareous matrix over a single eight-hour immersion cycle (procedure P3).
Results showing mass loss and pH change to single fragments of untreated matrix from specimen CIP-CBP16, each in 500ml of 2% weight: volume aqueous solution of three different acids (acetic, formic and sulphamic) in a single eight hour immersion cycle, run in triplicate (procedure P3). A final pH 2 indicates acid remains active.

Leaching of residual acid and soluble salt by-products is essential for the long-term stability of fossils following acid preparation (Lindsay 1987). The electrical conductivity of a water bath containing a sulphamic acid prepared specimen immersed in type 1 deionized water was monitored. Due to an initially low ion content, the type 1 deionized water exhibits a very low electrical conductivity (ASTM 2018), and thereby exerts a strong leaching force on the prepared specimen. This facilitates dissolution and movement of ions from areas of high concentration (within the specimen and remaining matrix) to areas of lower concentration (the deionized water). When the salt ions enter the deionized water from the prepared specimen, the electrical conductivity of the water increases (Hayashi 2014). Electrical conductivity thereby acts as a proxy for the rate of ion transfer between the prepared specimen and the deionized water and permits indirect monitoring of ions leaching from the specimen. However, the leaching effect is reduced as the ionic concentration of the water increases. Hence, during the 75 days of procedure P4, the electrical conductivity of the deionized water (i.e. the rate at which salts and/or residual acid leached into the deionized water) gradually reduced. Towards the end of procedure P4, electrical conductivity continued to increase, but by less than 1%. This can be attributed to continued low-level residual salt leaching but may have been the effect of concentration by evaporation of the water, although this aspect of the procedure requires further investigation.





Day	Conductivity (µS/cm)	Day	Conductivity (µS/cm)	Day	Conductivity (µS/cm)	Day	Conductivity (µS/cm)
1	0	17	175	40	304	58	346
2	18	18	182	43	305	59	353
3	34	19	188	44	306	60	355
4	48	23	224	45	309	61	357
8	96	25	234	46	319	71	374
9	107	29	262	51	331	72	376
10	116	30	262	52	334	73	376
11	126	31	263	53	336	74	376
15	162	38	294	56	338	75	377
16	168	39	299	57	345	78	380

Figure 1. Results from the leaching experiment (procedure P4). Electrical conductivity (in µS/cm) increase over an 11-week period when an approximately 7.1 kg and 3 l volume portion of the sulphamic acid prepared CIP-CBP16 (a partial ichthyosaur cranium) was immersed in type 1 deionized water. A, Graph showing the increase in electrical conductivity, until procedure P4 was terminated when the increase in conductivity levelled off to approximately 1% rate of change; B, the raw data from which the graph was constructed.

The preparators 'rule-of-thumb' following acid preparation is that a specimen should be rinsed under running water for at least three times the length of time the specimen has resided in the acid solution (Rixon 1976; Lindsay 1987). However, the results from procedure P4 indicate this is highly unlikely to remove sufficient acid and salt residues for effective long-term survival of acid prepared fossils. Prior to this work, acid prepared specimens were normally soaked in deionized water for a one or two-week period, with the deionized water changed two to three times during this time, prior to final drying. However, results presented here indicate that even this relatively extended period of leaching is unlikely to be sufficient to remove all acid/salt by-product residues. Indeed, salt blooms do occasionally occur on CIP specimens in the years following acid preparation (staff observations). Although the results from procedure P4 pertain to preparation with sulphamic acid, the technique of monitoring electrical conductivity of deionized water containing a chemically prepared specimen is equally applicable to those prepared in any aqueous acid solution.

Safety of sulphamic acid

As with all preparation techniques, the use of acids comes with risks to human health, as well as potential damage to the fossils being prepared. In particular, the use of mineral acids entails great risk to human health, but all acids come with health and safety concerns (e.g. Rixon 1976; Lindsay 1987). Hence acids must be treated with respect, and require: careful transportation and storage, with special cabinets to isolate acids from bases and other reagents; care when dispensed and mixed (requiring personal protective equipment); and adequate ventilation to prevent the build-up of toxic fumes. In addition, following acid preparation, spent acid needs to be safely disposed of, requiring neutralization and/or specialized acid-resistant pipework and disposal facilities, which depends on applicable local and national regulations. For these reasons, it is preferable to use organic acids, over mineral acids, for fossil preparation because they are safer to use, easier to control and less problematic to dispose of. Hence, with time, there has been a general trend away from the use of strong mineral acids towards the use of weaker organic acids, associated with a reduction in the acid concentrations used for fossil preparation (Whybrow 1985; Rutzky *et al.* 1994). This reduces risks to users and improves the quality of preparation by minimizing damage to specimens (Lindsay 1987), albeit with longer preparation times.

Human health

All acids are potentially dangerous to human health, and there are several ways of assessing risk. As health and safety regulations covering the use of acids vary between countries and institutions the details will not considered here, and this article should not be considered a source of safety information. Instead we concentrate on one simple proxy, the US NFPA 704 Hazard Identification Standard (NFPA 2007); however, it should be noted that this standard was developed to alert first responders to potentially hazardous substances and was not intended to be used to assess laboratory risks. The NFPA 704 Standard uses four colour-coded fields to convey hazard information: health (blue), flammability (red) and reactivity (yellow), each scaled from 0 (essentially no hazard) to 4 (extreme hazard); and additional information (white). Sulphamic, formic and acetic acids are all classified with a high health risk (3), although sulphamic acid is less flammable and less reactive than either formic or acetic acids (Table 1). Hence, sulphamic acid, as a crystalline solid, should be safer to transport and store compared to concentrated formic and glacial (undiluted) acetic acids, both of which are dangerous to handle. The liquid and vapour phases of formic and acetic acids can cause severe irritation to mucous membranes, and acetic acid can severely damage skin and formic acid can be absorbed through the skin (Le Berre 2013; Hietala 2016). Sulphamic acid is not toxic, but can cause irritation to eyes, nose and skin although its effects are more typical of a mineral acid (Metzger 2012).

Specimen safety

In addition to human health and safety concerns, acid preparation can entail considerable risks to the specimens being prepared (Lindsay 1987). Acid preparation can be difficult to control, because it largely acts unseen, on the surface of the specimen but also anywhere the acid solution can penetrate (e.g. through porous matrix; cracks; or natural porosity in the fossil bone). Risks to specimens include: acid attack to phosphates within the fossil bone due to inadequate consolidation or buffering; overly violent acid reaction, rapidly liberating CO_2 gas bubbles which exert considerable internal pressure on fossil and matrix; repeated emersions in aqueous solution that can lead to deformation due to repeated wetting (swelling) and drying (shrinkage) of clay minerals; overly rapid drying that can lead to cracking of matrix and/or the enclosed fossil specimen; and the removal of too much supporting matrix, which can leave a fossil too fragile for handling, study and storage (Rixon 1976; Jeppsson *et al.* 1985; Lindsay 1987; Rutzky *et al.* 1994).

The use of stronger acids (such as formic acid over acetic acid, or sulphamic acid over formic acid) has been preferred by some authors (e.g. Rutzky *et al.* 1994) because although the acid is stronger, the specimen requires fewer acid immersion cycles and this is considered less stressful to the fossil. Fewer immersions also require less handling and this reduces the potential for accidental damage to a specimen. However, conversely, the more aggressive chemical action of a stronger acid liberates CO_2 gas bubbles more rapidly within the specimen, potentially causing volumetric increases and specimen damage (Rutzky *et al.* 1994). Hence, the balance between acid strength and the number of immersion cycles is fundamental when deciding which acid to use for any particular fossil preparation project (Whybrow and Lindsay 1990; McCrae and Potze 2007). However, there are also practical and cultural differences when selecting which acid to use, with acetic acid generally preferred the UK and much of mainland Europe, and formic acid more commonly used in the USA (Rixon 1976; Lindsay 1987; Rutzky *et al.* 1994; Padilla *et al.* 2010; Hellawell and Nicholas 2012).

Sulphamic acid, as a stronger acid than formic or acetic acids, so this will speed up preparation, reduce staff time, and reduce the amount of spent acid to be disposed of: with potentially important environmental, health and cost considerations. With proper supervision, especially in the early stages of acid preparation, it should be possible to undertake longer chemical preparation cycle times, because the lower final pH of sulphamic acid indicates a greater part of the original acidity remains unspent, compared to formic and acetic acids (procedures P1-P3). In the CIP, preparators occasionally go beyond eight-hour acid bath cycles with sulphamic acid, especially in the early stages of preparation, carefully inspecting the progress of the acid on the specimen a minimum of every two hours.

Comments on sulphamic acid preparation

A key factor to consider is whether or not to undertake physical preparation, or whether remote imaging techniques could replace preparation entirely (e.g. Lautenschlager 2016; Racicot 2017). In the case of the CIP, specimens are used for both scientific study and museum display, and the income from visitors pays the running costs of the institution. Also the size, potential damage and cost of transporting specimens excessive distances, prohibits CT scanning techniques.

Experience with the sulphamic acid preparation of large vertebrates encased in a lime-rich matrix indicates that two of the most important aspects of acid preparation are: 1) the initial assessment of the specimen for the suitability of acid preparation, and 2) re-assessment of the specimen following the initial, short, low concentration, unprotected acid bath cycle (Lindsay 1986; McCrae and Potze 2007). Specific aspects that should be considered, before deciding how to continue, include: how much fossil bone is exposed; how fragile or deteriorated the exposed fossil is; and the number and size of fractures that will permit unseen acid ingress (and hence unpredictable action). Only when the preparator has fully addressed these points, can a preparation plan for the specimen be developed and implemented (Rutzky *et al.* 1994).

Another critical aspect of sulphamic acid preparation is the protection of newly exposed fossil bone with acid resistant consolidant, and the filling of cracks and crevices to minimize unseen acid ingress (Rutzky *et al.* 1994). After normal rinsing and air-drying, complete drying of the specimen is ensured by immersing the specimen in ethanol. The miscibility of ethanol with water, and its volatility (Kosaric *et al.* 2012), helps remove residual moisture from the specimen. Failure to sufficiently remove moisture can lead to a lack of adhesion, or whitening, of the acid resistant consolidant (McCrae and Potze 2007). After ethanol immersion and complete evaporation, the specimen is ready for application of consolidant. We use Paraloid B72 dissolved in ethanol (due to national level restrictions on the use of acetone), and this has proved to be effective as an acid resistant protective layer (Davidson and Alderson 2009) for sulphamic acid preparation. Depending on the porosity of the fossil, a 5% w:v coat of consolidant is applied, although priming the surface with ethanol prior to application reduces surface tension and improves consolidant penetration. If a 5% w:v consolidant solution does not adequately penetrate the bone, a weaker solution, or pure ethanol can be brushed onto the surface to assist penetration. Once the first layer is dry, one or more additional applications of 5% w:v consolidant are applied, and the process is completed by the application of 15% w:v Paraloid to develop an acid-proof barrier. This multi-stage acid protection process is repeated after each acid immersion cycle, with the existing and newly exposed fossil bone kept in excellent condition as the specimen goes through repeated acid bath cycles.

As sulphamic acid preparation nears completion, or once the acid has begun to expose delicate structures, such as sutures, surface ornament or sclerotic plates, the acid bath cycles can be shortened, or the acid concentration reduced. Halving the acid concentration from 4% to 2% w:v allows for slower, more delicate preparation work, and minimizes potential acid damage to the specimen. As with most acid preparation, the effectiveness of sulphamic acid can be enhanced by incorporating mechanical preparation, the Waller Method or thioglycolic acid for the removal of intractable matrix such as that rich in ferric iron (Blum *et al.* 1989; Whybrow and Lindsay 1990). Combined acid and mechanical preparation have the advantage that this further reduces the number of acid bath cycles (Table 5) and hence the stress of acid preparation on the specimen, although the potentially deleterious effects of mechanical preparation on delicate fossils need to be carefully considered (Padilla *et al.* 2010). Regular condition checking is essential, as is documentation of the whole acid treatment process.

Quality of sulphamic acid preparation

Trials with sulphamic acid began in 2002. Initially, the acid preparation protocol used acetic and formic acids in combination with sulphamic acid (Padilla *et al.* 2010) but after comparative tests, the results of which are reported here, sulphamic acid has been used exclusively. Sulphamic acid has been used to prepare several important large marine vertebrate fossils with excellent results, including: the protostegid turtle *Desmatochelys padillai* Cadena and Parham 2015 (the holotype CIP-CBP01, and other specimens CIP-CBP13, 15, 39, 40); the Sandownid

Acid strength (weight: volume)	CIP-CBP4	CIP-CBP3
	Acid preparation only	Mechanical and acid preparation
4%	15	7
2%	6	3

Table 5. Subjective comparison of acid-only and acid-mechanical preparation for two large marine vertebrate fossils from Colombia.
The number of preparation cycles undertaken on two large marine vertebrate specimens using sulphamic acid (CIP-CBP4, a long-necked plesiosaur), and sulphamic acid preparation augmented with mechanical preparation between acid bath cycles (CIP-CBP3, a pliosaurid). Acid strength was reduced as a greater volume of fossil bone was revealed.

turtle *Leyvachelys cipadi* (CIP-CBP71) Cadena 2015; the non-brachiosaurid titanosauriform dinosaur *Padillasaurus leivaensis* Carballido *et al.* 2015 (see also Mannion *et al.* 2017) (MJACM 4); and the opthalmosaurid ichthyosaur *Muiscasaurus catheti* Maxwell *et al.* 2016 (CIP-CBP74).

Future work

This work is a provisional study on the efficacy of sulphamic acid for the preparation of large vertebrate fossils, and study of salt and acid residue leaching following sulphamic acid preparation. Future work could include standardizing the surface areas of matrix samples for acid preparation, although it remains impossible to control for matrix inhomogeneity (Padilla *et al.* 2010), and the pH of the acids in future work should be more precisely measured (e.g. in 0.1 pH increments). In terms of leaching, similar experiments need to be undertaken on specimens prepared in formic and acetic acids to see if the same high level of ion removal occurs, as would be expected from the results presented here. In addition, tests should be repeated with regular replacement of the type 1 deionized water to understand continual salt and acid leaching, and the increased concentration of ions in solution as a result of evaporation from the water bath also needs to be controlled for.

Conclusions

Sulphamic acid is a stronger acid than formic and acetic acids (Table 1), the latter two of which are at present the acids most commonly used for the preparation of fossils preserved in a calcareous matrix. Comparative tests on the preparation of large marine reptiles from the Paja Formation Lagerstätte of Central Colombia show sulphamic acid performs as well as formic acid, and more rapidly than acetic acid, in terms of the number of acid bath cycles required for removal of the same volume of matrix. Sulphamic acid retains its acidity longer than acetic or formic acids, and can therefore be used for more immersion cycles, which reduces the amount, and cost, of spent acid solution disposal. Under NFPA 704 Hazard Identification Standard (NFPA 2007) sulphamic acid is overall less hazardous than formic or acetic acids, reducing the risks of transport, storage and potentially working with these hazardous substances. Given increasingly stringent health and safety regulations, concerns over laboratory staff wellbeing, and ongoing consideration of environmental impact, sulphamic acid is worth considering in a facility undertaking acid preparation of large vertebrate (and other) fossils. The capacity of sulphamic acid to differentiate fossil from calcareous matrix, in the presence of a phosphate buffer, is comparable to that of the established formic and acetic acids, producing highly detailed preparation of fossil vertebrate material. The process of leaching acid and evolved salt residues following acid preparation is critical for the long term survival of acid prepared specimens. Our results indicate a much longer period of leaching than currently routinely applied is required to ensure maximum removal of residual acid and evolved salts following acid preparation, and strongly reinforces the long held preparators adage of 'acid short-water long'.

Acknowledgments

This contribution is dedicated to the Memory of C. B. Padilla Bernal, with whose ideas and work this article has its beginnings, and who died unexpectedly on 12th November 2013. Thanks are extended to R. Gómez-Cruz (formerly Universidad de los Andes, Bogotá) for discussion and revision of acid chemistry; to E. S. Gaffney, J. Maisey, M. Norell (American Museum of Natural History); J. Mason (University of California Museum of Paleontology) for discussion and advice; M. L. Parra and J. de D. Parra (CIP) for their laboratory skills; and A. Davidson (American Museum of Natural History) is thanked for reviewing a pre-submission version of the manuscript. LFN was funded by a 'Fondo de Apoyo para Profesores Asistentes' grant (FAPA no. P12-160422.006/01) and the manuscript completed during the tenure of a project entitled 'The Paja Formation largestätte of the Alto Ricaurte: access, palaeoenvironment and taphonomy' and a Semestre de Trabajo Académico Independiente (STAI) awarded by Universidad de los Andes, Bogotá. We thank an anonymous reviewer for comments that considerably improved the original manuscript, and Matthew Parkes for prompt and efficient editorial assistance.

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PREHISTORIC HUMAN MATERIAL IN THE NOTTINGHAM NATURAL HISTORY MUSEUM, AND THE CRESWELL CRAGS MUSEUM AND HERITAGE CENTRE

by Nicole A. Mantl, BSc

Mantl, N. 2019. Prehistoric human material in the Nottingham Natural History Museum, and the Cresswell Crags Museum and Heritage Centre. *The Geological Curator* 11 (1): 93-106.

The Creswell Crags Museum and Heritage Centre (CCMHC) and the Nottingham Natural History Museum, Wollaton Hall (NOTNH) both curate collections of prehistoric human material that have undergone limited documentation. The condition of current records demanded revision, which this study will perform. Reported here are nine cranial, and five postcranial Neolithic and late Iron Age human bone specimens, as well as two teeth, collected at the CCMHC from the late 19th century excavation of the caves of the gorge and nearby area. Three crania, and three post cranial human bone fragments dating to the late Pleistocene are present among the NOTNH collection; these originate from various locations in the East Midlands. This paper offers a revised account of the material, providing detailed osteological descriptions, and biological profiling of sex, age, pathology and taphonomy; where possible historical backgrounds, and radiocarbon dating information are included in this report. Overall the specimens were found to be in fair condition, while the collections' records of the material required minor corrections.

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Introduction

This study provides an anthropological evaluation of the human material held at the Nottingham Natural History Museum, Wollaton Hall, (NOTNH) and the Creswell Crags Museum and Heritage Centre (CCMHC), as well a review and clarification of the related documentation.

Museums are often unable to fully catalogue and accurately describe all of the specimens they hold due to the large amount of material stored in their collections, and other factors such as changes in curatorial staff (Owen F., pers comm, 2018). Specimens are sometimes lost or forgotten on museum storage shelves, and accounts of their provenance change over time, leading to inconsistent or incomplete information (e.g. Robin Hood Cave 1 specimen discussed below). It is also the case that some specimens happened to not be reported in the literature despite their discovery along with other material, as will be discussed later. While retrieving part of the material for this study, uncatalogued specimens were also identified and included. This study highlights the need for full descriptions of material that is discovered, to help prevent later confusion over context or identification.

As part of this investigation, several different accounts of the events that occurred during the numerous excavations of the Creswell Crags caves were collected. Many early papers, in particular those by Mello (1875, 1876, 1877), Dawkins (1877) and Dawkins and Mello (1879), did not produce detailed information regarding the human material retrieved, since they only provided brief mentions and notes. Later reports by Campbell (1970, 1977) and Jenkinson (1984), partially clarified the chronology of the research conducted around the Creswell area.

Additionally, radiocarbon dates for three of the specimens studied have been published (Gowlett *et al.* 1986; Hedges *et al.* 1991; Hedges *et al.* 1998). Unfortunately, some of the remains have not yet been dated, and it may no longer be possible to perform radiocarbon analysis, due to their treatment with isinglass. Isinglass is a gelatinous substance, similar to collagen, used to seal specimens and prevent the material from deteriorating but may also prevent any attempt at radiocarbon dating, because the varnish may have preserved carbon-containing contaminants, producing unreliable dates (Brock *et al.* 2018). Ultimately these specimens' temporal origins will remain ambiguous.

Material and method

The NOTNH Museum at Wollaton Hall houses a collection of ~40,000 fossils (Turner 1993, 2000; Smith 2015). The material studied consists of items from various localities in Nottinghamshire and Derbyshire, including Attenborough, Colwick Hall (Nottingham) and Creswell Crags. None of these specimens has been radiocarbon dated, and the small amount of information recorded is mainly inferred from what is known about the stratigraphy of these localities. The collection at the CCMHC contains a number of human remains including those from Whitwell Quarry Long Cairn, published by Vyner and Wall (2011), and not considered further here.

Each item is described including physical appearance, and features of potential interest in determining pathologies and other factors. Measurements of all specimens can be found in the report lodged with the collections. With regard to sex and ontogenetic age of the specimens, determinations or estimations were recorded where significant characters could be used. With the exception of a juvenile ischium, all determinations were made based upon the cranium, also following Bass (1995). Definitions for dentition follow Hillson (1996), while tooth development was scored according to Schour and Massler (1941) (as summarised in Hillson 1996), tooth wear was scored according to Smith (1984) (as summarised in Hillson (1996)), and age was estimated using Brothwell (1981). The osteological examination was then integrated with any published radiocarbon dating and stratigraphic data.

Nottingham Natural History Museum (Wollaton Hall) specimens

All provenance data is taken from the NOTNH specimen labels and database unless stated otherwise.

A common characteristic of the examined bones is a shiny surface due to isinglass treatment and a dark brown patina likely caused by soil staining or waterlogging. The specimens of crania, examined during this study, exhibit what could potentially be bossing caused by the pressure forced on the bone by prolonged burial in sediment, resulting in deformation, horizontal compression and lateral widening of the skull.

Attenborough

Attenborough is located on the Trent Valley Formation, specifically the Holme Pierrepont Sand and Gravel Member (British Geological Survey [no date]). Deposited during MIS (Marine Isotope Stage) 2 and MIS 1, this period spans approximately the last 29,000 years during the final period of the last glacial stage, the Devensian, and the current, Holocene, interglacial (Lisiecki and Raymo 2005; Lisiecki 2018). The Holme Pierrepont Terrace was later covered by Holocene (MIS 1, since 14,000 BP) alluvium, i.e. a younger deposit, due to changes in flood frequency (Howard *et al.* 2011). It is unlikely than any human presence could have been encountered before then due to the severe climatic conditions during the Stadial. It is, however, difficult to narrow down the age of the specimen from this locality without further geological analysis.

NOTNH FS4850 Human cranium (Figure 1)

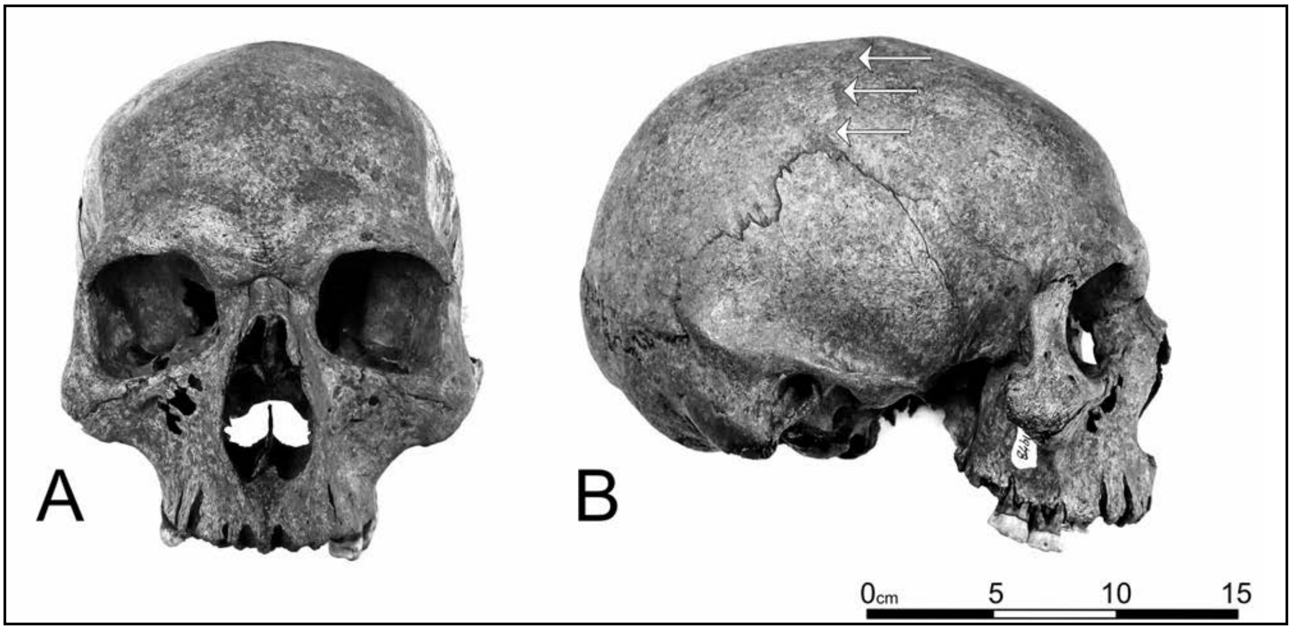


Figure 1. NOTNH FS4850. Cranium of the 'Beaker Man' from Attenborough, Nottinghamshire. A: norma frontalis. B: right norma lateralis; the arrows indicate the unusual coronal suture.

The cranium is consistent with a male individual, as suggested by a prominent mastoid process and brow ridge, The dental wear on the present dentition was scored as Smith stage 5 for both first molars, and stage 4 for both second molars and the left fourth premolar; this indicates an estimated age of around 25-35 years. Both first molars present carious lesions on the buccal surface of the crown. This individual is thought to date to around 4,000 years ago (according to the NOTNH database), probably as a result of the contemporaneous discovery of pottery fragments, known as beakers, which led to the nickname 'Beaker Man'. This particular type of pottery dates to approximately 2,300 BCE and was also found with the famous Amesbury Archer near Stonehenge (Salisbury Museum [no date]; Olalde *et al.* 2018).

The structure of the specimen's cranial sutures is relatively rare in adult specimens, and a full metopic suture such as this is known to occur in 1.25%-30% of individuals, depending on the population (Kumar and Rajshekar 2015; Tunali 2016). Instead of the development of a 'T-shaped' suture line at bregma, the sagittal and coronal sutures of the specimen form a cross, which result in a shortening of the occipital and both parietal bones, shifting their position towards the back of the cranium (Figure 1B). Additionally, three small accessory bones are present along the lambdoid suture, one on the left and two on the right.

Colwick Hall, Nottingham

Located on the same River Trent Terrace as Attenborough, the material from Colwick Hall was again recovered from the same Holocene alluvium. It is suggested (from the NOTNH database) that the material from Colwick Hall could be from the latest Pleistocene, but it is ultimately impossible to further narrow down the age of the specimens.

NOTNH FS12422 Human skullcap (Figure 2)
The incomplete skull consists mainly of the cranial vault: the left temporal bone, frontal bone and occipital bone are only partially preserved. The prominent brow ridge and the lack of mental bossing suggest that the individual could have been a male individual. The individual is certain to have been an adult, however his age could not be refined further. A detailed examination of the sutures revealed a partial fusion of only the sagittal suture; internally, all sutures appeared to be fully fused.

A small lesion near the right lambdoid suture is present and appears to have more likely been caused by a form of ante-mortem or post-mortem injury rather than by taphonomic or post-excavation damage. This is made apparent by the fact that the fracture lines are the same colour as the rest of the bone. The dark brown to black colouration, which is usually associated with humic acids present in the soil, could only be present if the fracture was exposed to the soil prior to excavation (Dupras and Schultz 2013).

NOTNH FS12423 Human skullcap (Figure 3)
This specimen appears to belong to a probably male individual as demonstrated by the prominent brow ridge and mastoid process. Once again, the cranium is incomplete, missing all facial bones except for the sphenoid. The specimen represents an adult individual, but sex could not be definitely determined. An accessory bone is present on the squamous suture, joining the right sphenoid bone to the parietal.

NOTNH FS12412 Human tibia (Figure 4)
The tibia belongs to an adult individual as deter-

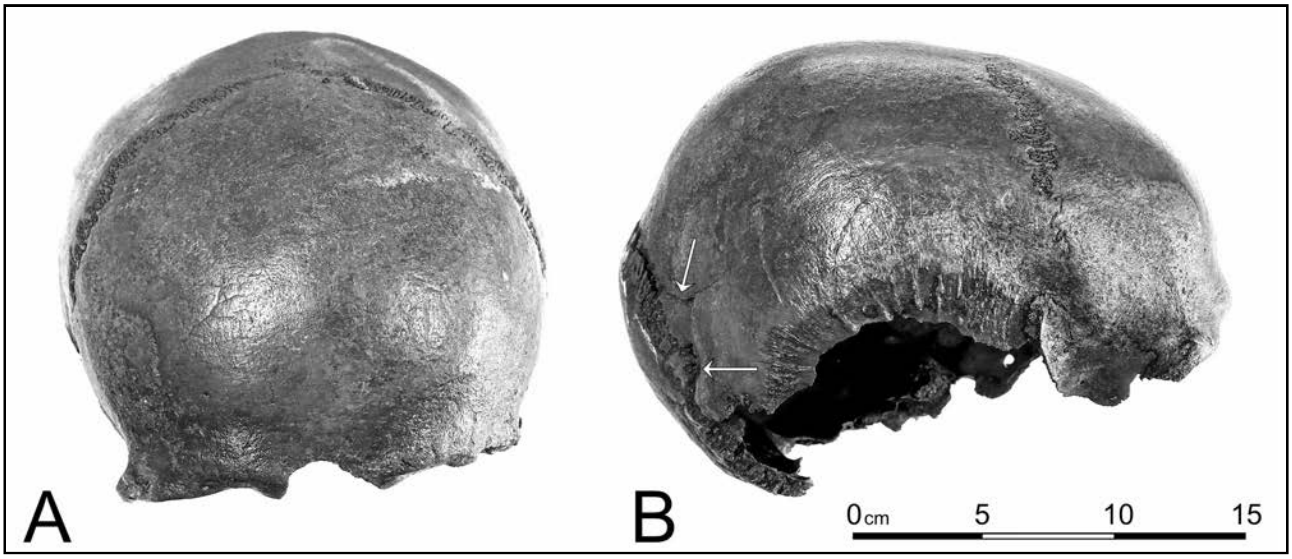


Figure 2. NOTNH FS12422. Human calotte from Colwick Hall, Nottinghamshire. A: norma frontalis. B: right norma lateralis; the top arrow indicates a fracture line; the bottom arrow indicates an accessory bone.

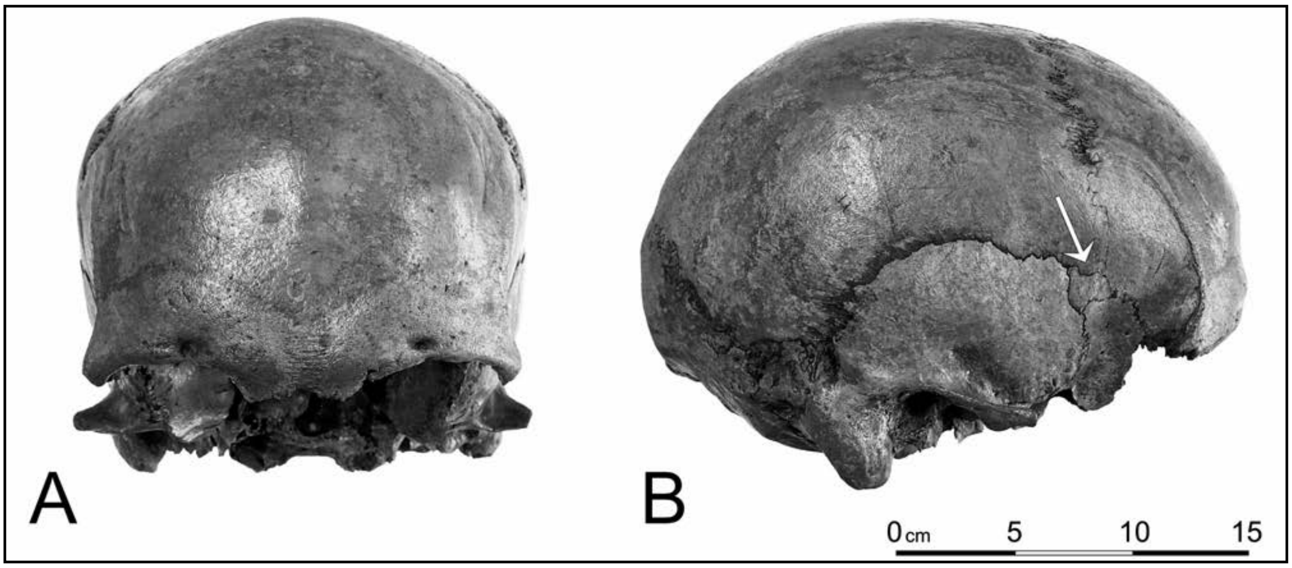


Figure 3. NOTNH FS12423. Human cranium from Colwick Hall, Nottinghamshire. A: norma frontalis. B: right norma lateralis; the arrow indicates an accessory bone between the temporal, frontal, parietal and sphenoid bones.

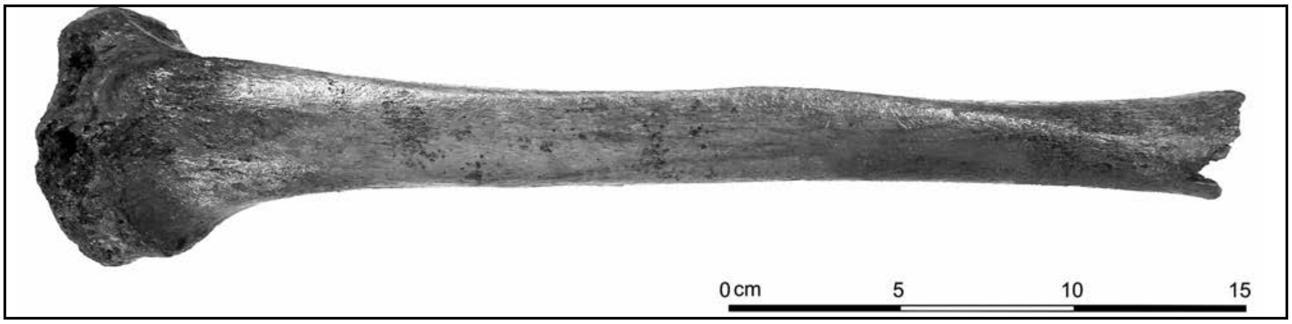


Figure 4. NOTNH FS12412. Human tibia from Colwick Hall, Nottinghamshire. Frontal view.

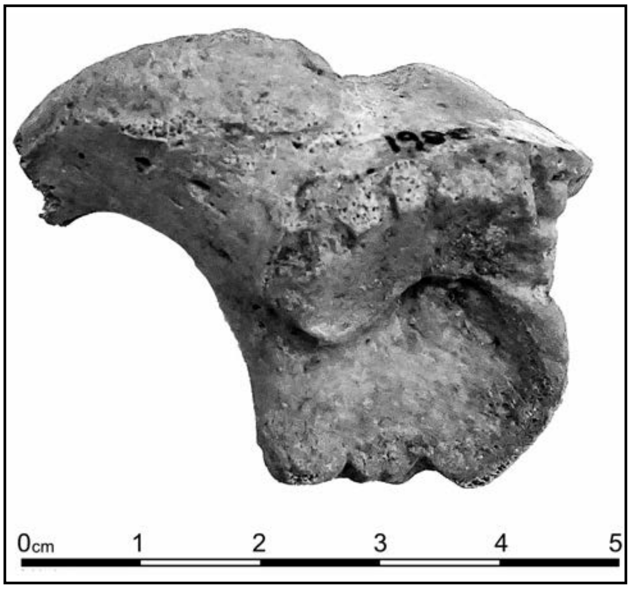


Figure 5. NOTNH FS4341. Human ischium from Creswell Crags. Ventral view showing original marking '1988'.

mined by the complete fusion of the proximal epiphysis. The bone has been broken at the end of the anterior crest towards its distal end and there is also slight damage to the proximal end. From its sequential number and identical preservation, it may be directly associated with the previously examined human vault (FS12422).

Creswell Crags

In the NOTNH collection there are two human specimens from Creswell Crags (Bestwick and Smith 2015).

NOTNH FS4341 Human ischium (Figure 5)
Mello excavated a right juvenile ischium which he probably bequeathed to the NOTNH museum in 1887 (Bestwick and Smith 2015). The date on the label accompanying the specimen would rather indicate that the acquisition occurred around 1988, yet there is no way of being certain without access to NOTNH acquisition documents.

The child could not have been older than five years of age, based upon the developmental stage of the bone. All ossification surfaces are still clearly visible, and the acetabulum is in its initial phase of formation.
Roger Jacobi, whose handwriting was recognised on the labels preserved along the specimen (Owen F., pers comm, July 2018) probably determined the archaeological age of the ischium and assigned it to the Upper Pleistocene period, according to its stratigraphic location.

NOTNH FS4315 Human ulna (Figure 6)

Figure 6. NOTNH FS4315. Human ulna from Creswell Crags. Lateral view showing original label written by J. Magens Mello.

Mello also recovered a partial left ulna, which is missing the distal half and the proximal epiphysis (Figure 6). It is possible that the bone was found in the talus outside the entrance to Robin Hood Cave by Mello (1877, p580), who only notes that 'small fragments of human bones' were found, and later mentioned by Dawkins (1877, p600). However, no identification number was found that could be used to confirm that this is one of the human fragments recovered in 1877.

Creswell Crags Museum and Heritage Centre specimens

The Creswell Crags Museum and Heritage Centre (Figure 7) is located in the East Midlands not far East of Worksop. Originally excavated by Victorian explorers, beginning with the Rev. J. Magens Mello, T. Heath and W. B. Dawkins, Creswell Crags is well known for being the site of some of the earliest examples of Upper Palaeolithic carvings and man-made tools in the British Isles (Pettitt 2003; Pike *et al.* 2005; Bahn and Pettitt 2009). However, concerns later arose surrounding the excavation techniques employed and the authenticity of certain artefacts recovered by these 19th century excavations. In particular, a sabretooth cat tooth discovered by Dawkins in 1876 and the engraving of a horse on the fragment of an animal rib discovered by Mello during the same excavation (White 2016).

As with the specimens held at NOTNH, shiny isinglass treated bone is again represented in the specimens from CCMHC, unless otherwise stated. Similarly, patina staining is seen in varying degrees of intensity from light brown to almost black; this is due to the humid and wet conditions in the caves of Creswell Crags and the surrounding area. Flooding of the caves was a frequent occurrence and is also known to have interrupted the frequent inhabitation of the cave by hyenas (Dawkins 1876).

Ash Tree Cave

Ash Tree Cave was discovered by Leslie Armstrong in the late 1930s and he continued his excavations in the 1950s. Armstrong died in 1956 and no written record of the excavations has been published to describe the origins of the artefacts and remains he discovered. Similarly, only unpublished notes remain from two further excavations, McBurney in 1959 and an unpublished investigation by West and Riley (1959-1960).

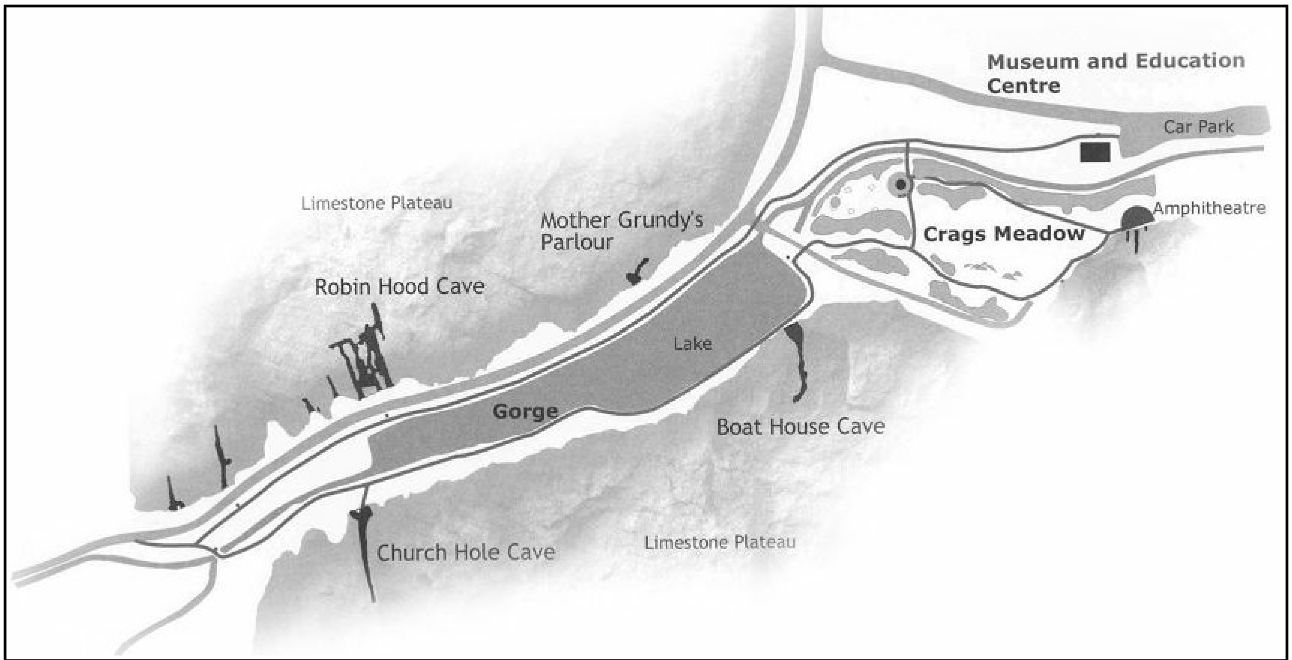


Figure 7. Map of the Creswell gorge outlining the position of each cave. Image courtesy of Creswell Crags Heritage Trust.

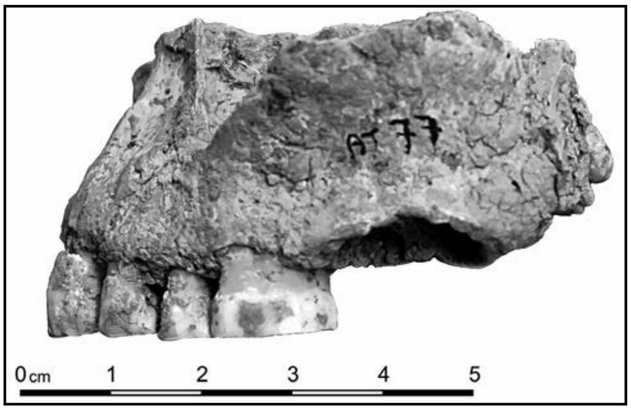


Figure 8. CWCHT AT77. Fragment of human maxilla from Ash Tree Cave. Left labial view showing embedded teeth.

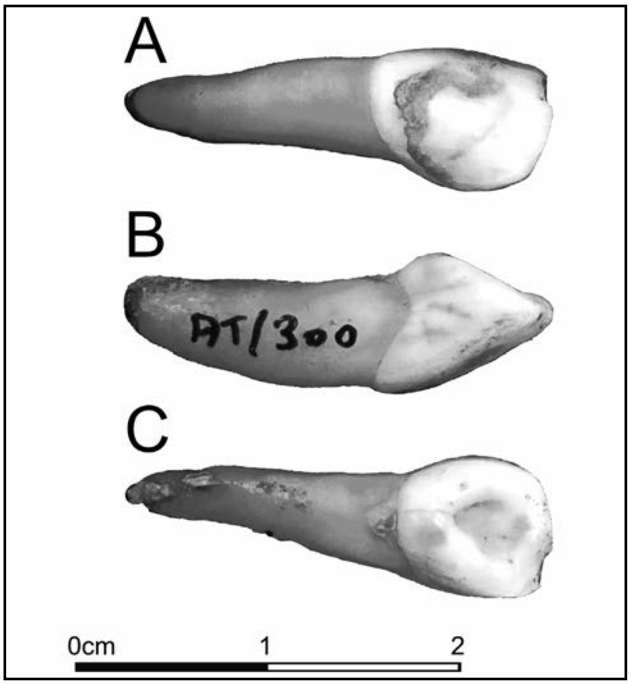


Figure 9. CWCHT AT-300. Human incisor from Ash Tree Cave. A: labial view. B: occlusal view showing marking 'AT/300'. C: lingual view.

Everything that is known about Ash Tree Cave derives from Armstrong's published work. In all probability, the inhabitation of the cave can be traced to the Mid-Late Devensian (Armstrong 1939; Jenkinson 1984).

CWCHT:AT-77 Fragment of partial human maxilla (Figure 8)

Acquired in 1979, the discovery of this fragment is attributed to Paul Mellars, who was an assistant during the second excavation of Ash Tree Cave in the 1970s. It is not known which excavation this specimen came from as no record of archaeological digging occurring during those years could be found. The bone was recovered alongside a soil sample with an identical label, although this was not analysed for this study. The fragment is still covered in sediment and has an unusual brown, almost black, patina.

The label attached to the fragment is inaccurate, as a canine was misidentified for an additional premolar. The left canine, third and fourth premolars, and first molar are present and are in fair condition, presenting signs of moderate dentine exposure on the canine (Smith stage 4) as well as the third and fourth premolars (Smith stage 5), and severe wear on the molar (Smith stage 7). From the wear pattern on the molar, the age of the individual was estimated to be around 35-45 years.

CWCHT:AT-300 Human incisor (Figure 9)

Very little information is known about this 1979 discovery. Wright is reported as the finder, but the circumstances are unclear. This right first incisor is of the permanent dentition and is fully formed and presents slight occlusal wear (Smith score 2) (see Figure 9C). Over time, the crown and the root have both assumed a yellow, almost orange coloration. There is presence of moderate calculus on the crown.

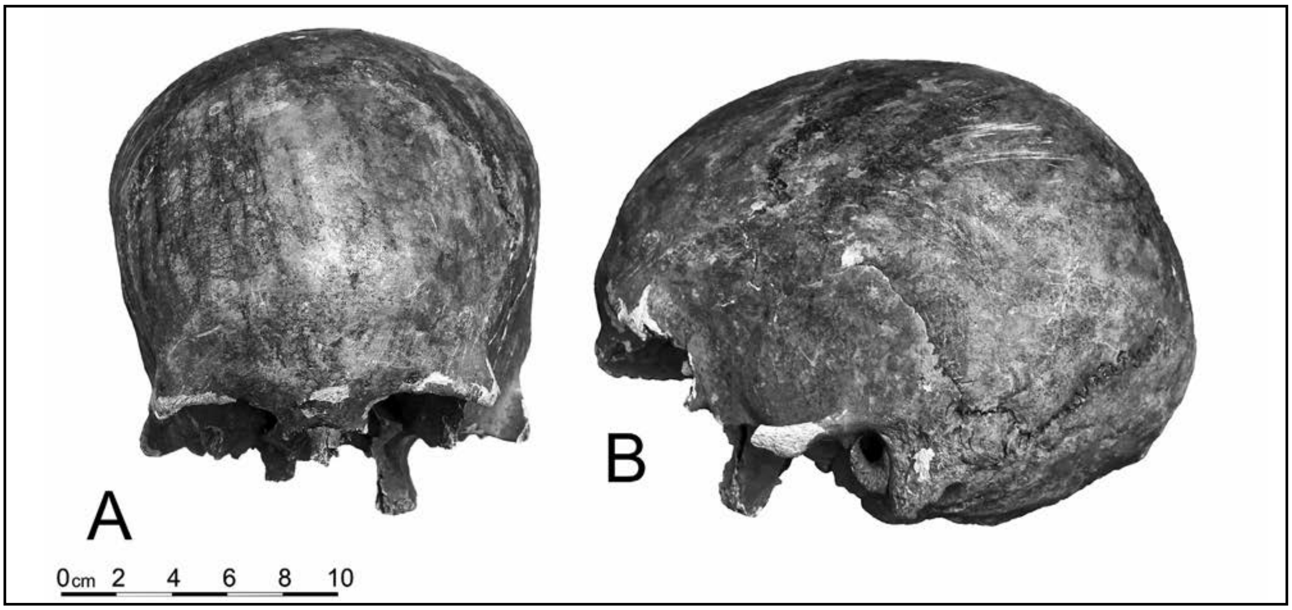


Figure 10. NT-1 (?). Human cranium from Higham Ferrers Quarry. A: norma frontalis. B: norma lateralis.

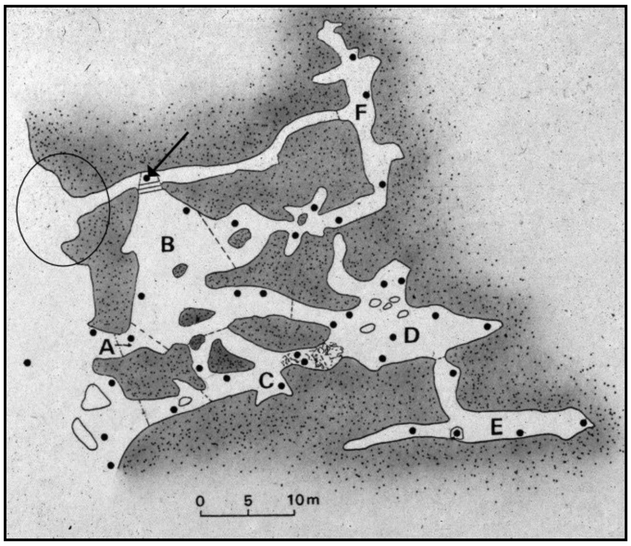


Figure 11. Ground plan of Robin Hood Cave. The circle indicates the location where RH-23 was found while the arrow indicates the location of the main burial site in Zone B. Zones A and B were excavated by Mello and Dawkins in 1875-76. Zones C, D, E and F were excavated by Laing in 1885. Zone O was examined by Campbell in 1969. (Image Terrell-Nield 1985)

Higham Ferrers Quarry, Northamptonshire

NT-1 Human neurocranium (Figure 10)

Despite a short identification label written on the cranium, no information was found in the CCMHC database regarding this specimen, its discovery, or other related remains. All cranial bones are present, excluding the zygomatic and the entire surface of the bone is heavily stained orange by the iron-rich quarry soil. The prominent mastoid process and brow ridge are more indicative of male traits.

Robin Hood Cave

Robin Hood Cave has been subjected to several excavations, conducted to fully explore the intricate system of chambers and tunnels that form it (Figure 11). Mello (1877) reported the recovery of twenty-six Holocene human specimens. Laing (1890) reported the recovery of five human specimens in 1889, some of which are now lost and little to no record of his research can be found (Jenkinson 1984). Campbell (1970) and Jenkinson (1981) both directed excavations respectively of the entrance and inside of the Western chamber; both reported additional human fragments, which are discussed in this report (Jacobi 2004; Jenkinson 1984). The location of the original burial (Figure 12) is indicated by the arrow over the stairs in Figure 11. All except one of the fragments, which was discovered in situ, were unearthed from the 19th century spoil. Which was deposited near the entrance to the cave, probably by Dawkins and Mello. Anyone exploring the spoil and the cave after them would have been presented with an inverted contextual sequence.

Figure 12. Image of the burial site in Robin Hood Cave where most of the human material examined in this paper was recovered. The location is no longer accessible as a staircase and platform have been built over it. (Photograph Terrell-Nield 1985)

From the fragments excavated in 1969, Campbell (1977) concluded that they were all part of a single individual, a young adult male (23-30 years old) whose head had been severed by cannibals and served as a trophy of sorts.

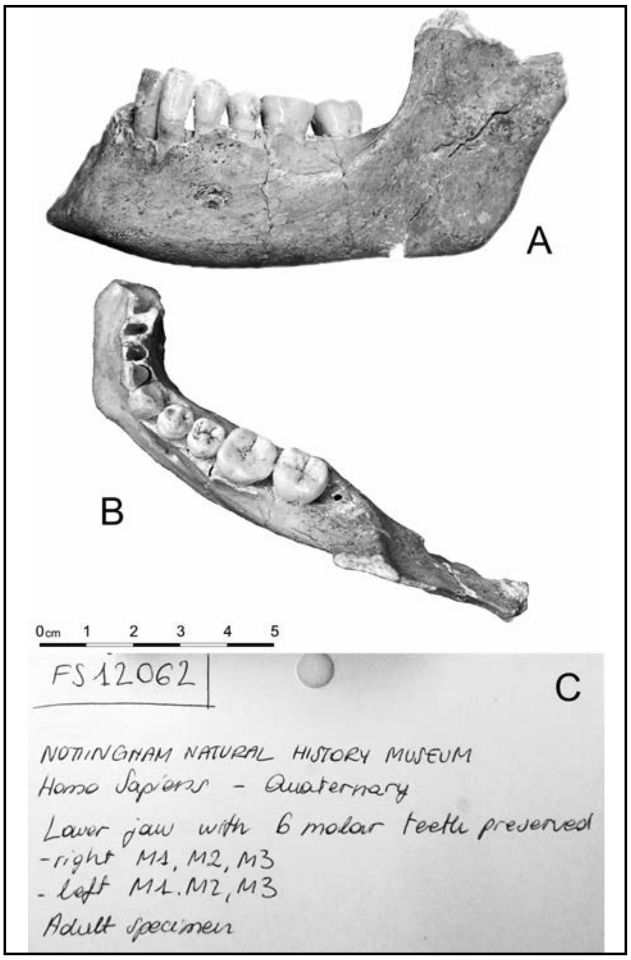
The cave itself is mainly composed of magnesium limestone, containing high levels of iron. The latter is often found to cause staining on organic material that is buried in the deposit. This is responsible for the light yellow/brown patina present on the majority of the specimens that have been examined in this paper.

CWCHT:RH-23 Human mandible (Figure 13)

This specimen was discovered by two schoolboys in 1975, who dug a metre into the travertine layer in the western chamber of Robin Hood Cave (Jenkinson 1984; Jacobi 2004). The bone was later determined to be from the Devensian period, as supported by further research strongly indicating an Early Upper Palaeolithic burial (Oakley 1908; Jenkinson 1984).

The mandible is not in the original condition in which it was recovered and reassembled, as it the mandible used to be complete with both rami (Jenkinson 1984, Plate 3).

The specimen represents a young adult, as determined from the lack of a third molar, and there are only initial signs of alveolar eruption. The first and second molar, the premolars, the canine, and the second incisor are all present and in good condition. No wear (Smith stage 1) can be seen on the second molar, third and fourth premolars, while there is pin-point dentine exposure (Smith stage 3) on the first molar and slight dentine exposure (Smith stage 3) on



FS12062

NOTTINGHAM NATURAL HISTORY MUSEUM
Homo Sapiens - Quaternary
Lower jaw with 6 molar teeth preserved
-right M1, M2, M3
- left M1.M2, M3
Adult specimen

Figure 13. CWCHT RH-23. Human mandible from Robin Hood Cave. A: left lateral view. B: occlusal view. C: new label produced for specimen RH23 by the author.

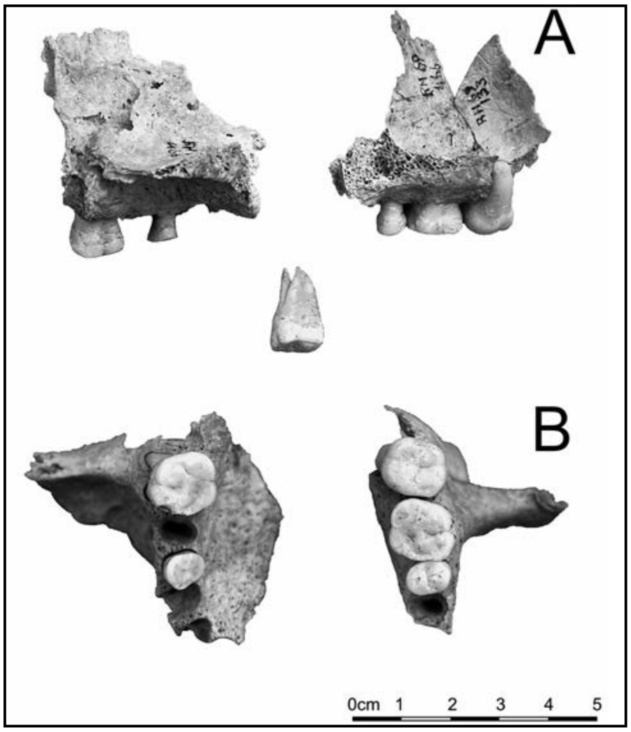


Figure 14. CWCHT RH-24. Fragments of human maxilla and tooth from Robin Hood Cave. A: lingual view of fragments showing old markings and one side of the third upper right molar. B: occlusal view of the two fragments.

the canine and second incisor. The tooth wear patterns further suggest that the individual would have been no older than 17-20 years of age at the time of death, which is not too far from the age determined from the third molar developmental stage of 16 years of age.

A first radiocarbon dating, requested by Jenkinson, determined that specimen OxA-736 was from the late Iron Age period (2020±80 BP) (Gowlett *et al.* 1986, Charles and Jacobi 1994). A decade later, upon resubmission of the specimen by Jacobi, it was found that sample OxA-6581 was almost certainly of Early Roman age (1785±50 BP), contradicting the stratigraphic correlation with the surrounding late Devensian sediment (Hedges *et al.* 1997).

CWCHT:RH-24 Human maxilla and tooth (Figure 14)

The fragments of this maxilla have a light brown colour, they are very light in weight and are heavily decalcified and present no sign of isinglass treatment.

The stage of wear on the molars would indicate an age of about 25 years, more likely in an intermediate stage between 20 and 35 years of age (Brothwell 1963). Supporting this, the presence of a fully developed loose third upper right molar would indicate an individual older than 19 years of age; additionally, the wear pattern on the molars suggests that the individual was at least between 17 and 25 years of age. There are signs of blunting (Smith stage 2) on the right third and second molar, while dentine is discretely exposed (Smith stage 4) on both first molars, moderately exposed on the right fourth premolar (Smith stage 3) and more strongly exposed on the left third premolar (Smith stage 5). There is differential wear between the right and left fragment; this variation could be explained by a pathological mis-alignment, something resembling a crossbite, or by a preferred chewing side. All teeth show signs of slight presence of supragingival calculus and the cusp of Carabelli is present on both first molars.

CWCHT:RH-25 Human occipital and sphenoid

Little is known about this specimen besides its original label and who it was discovered by. There is no sign of varnish being used to protect the bone. Unfortunately, there is significant damage to the exterior exposing the trabecular bone on the inside. According to the online records (these were available as of April 2018, a later update to their website made this information unavailable) of the bone it was originally identified as part of the pelvis (Creswell Crags [no date]).

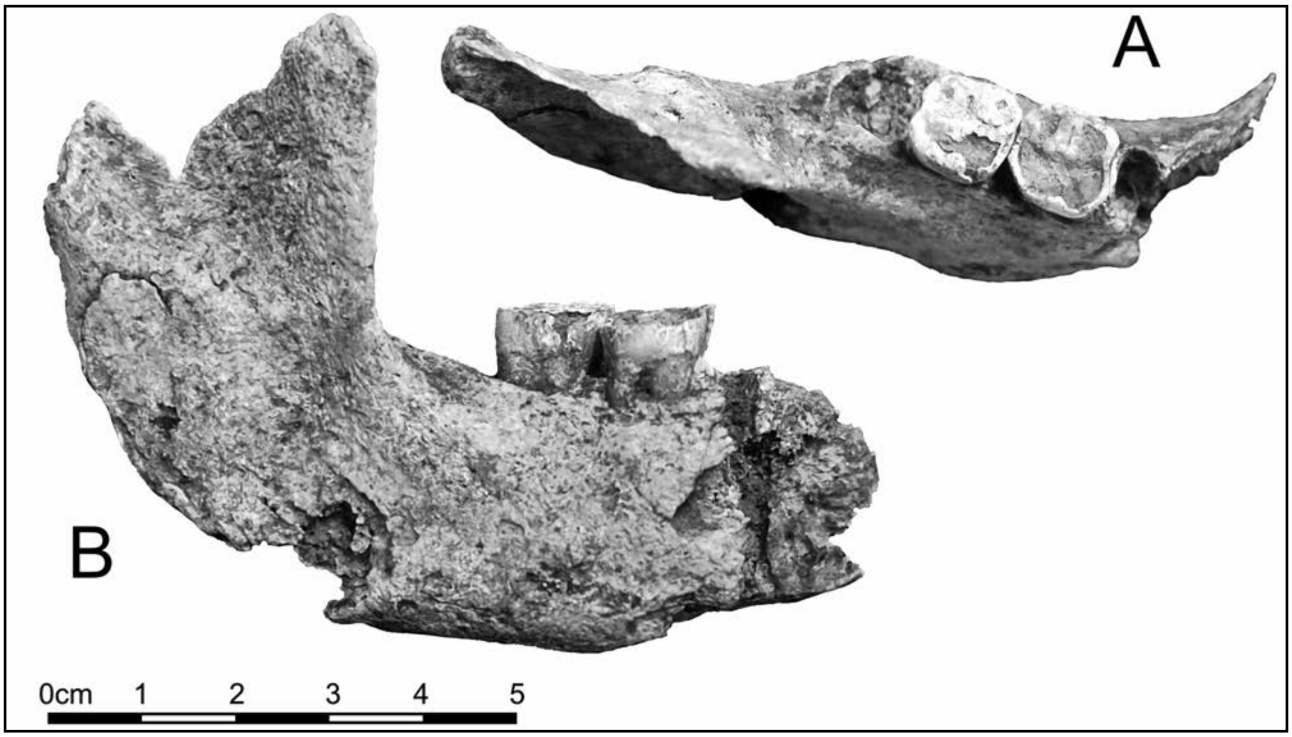


Figure 15. CWCHT RH-26. Human mandible from Robin Hood Cave. A: occlusal coronal view. B: labial view of fragment.

The current examination identified it as part of the occipital, specifically the basilar portion, and still attached to a small fragment of the sphenoid body. The presence of the occipital condyle and part of the rim of the foramen magnum confirms this identification.

CWCHT:RH-26 Human mandible (Figure 15)
This fragment consists of the right arch of a mandible containing the first and second molars. The dentition shows considerable wear of both the enamel and dentine below, leading to a flattened occlusal surface (Figure 15). The individual was an adult around the age of 25-35 years, as indicated by the tooth wear (Smith stage 6 for the first molar and stage 5 for the second molar) and supported by the presence of the socket for the third molar.

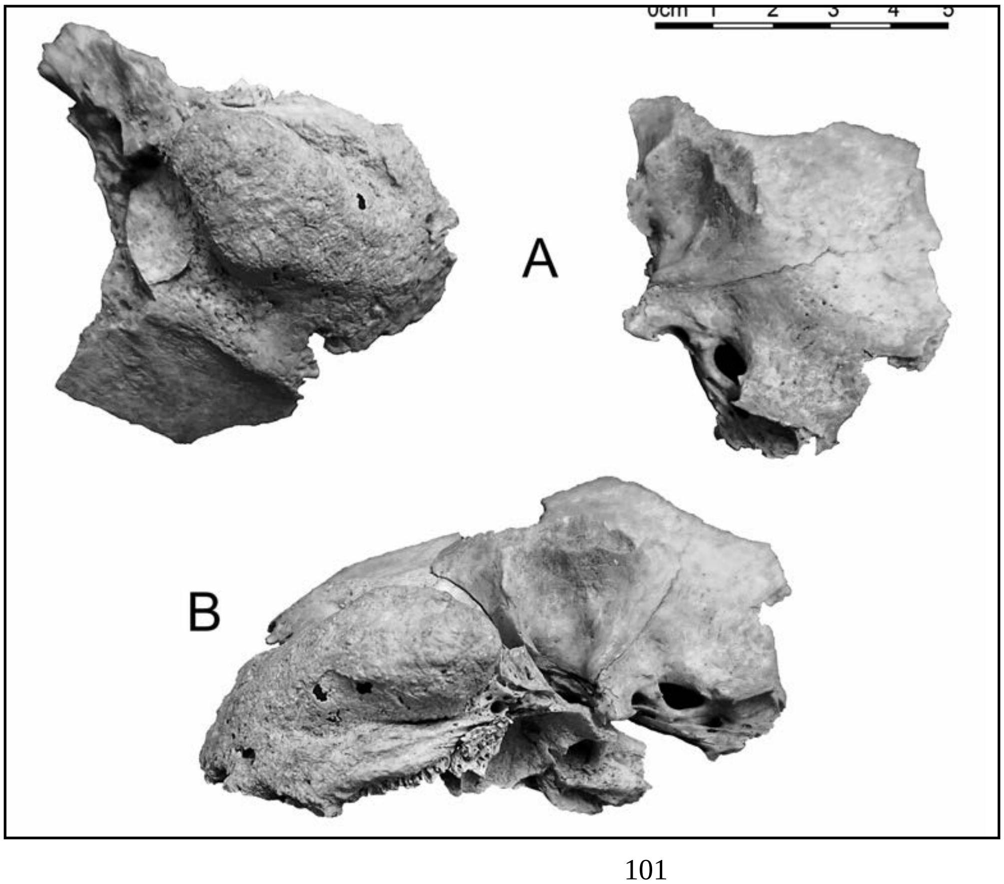


Figure 16. CWCHT RH-28. Fragments of human temporal from Robin Hood Cave. A: ectocranial view of the two fragments. B: fragments refitted.

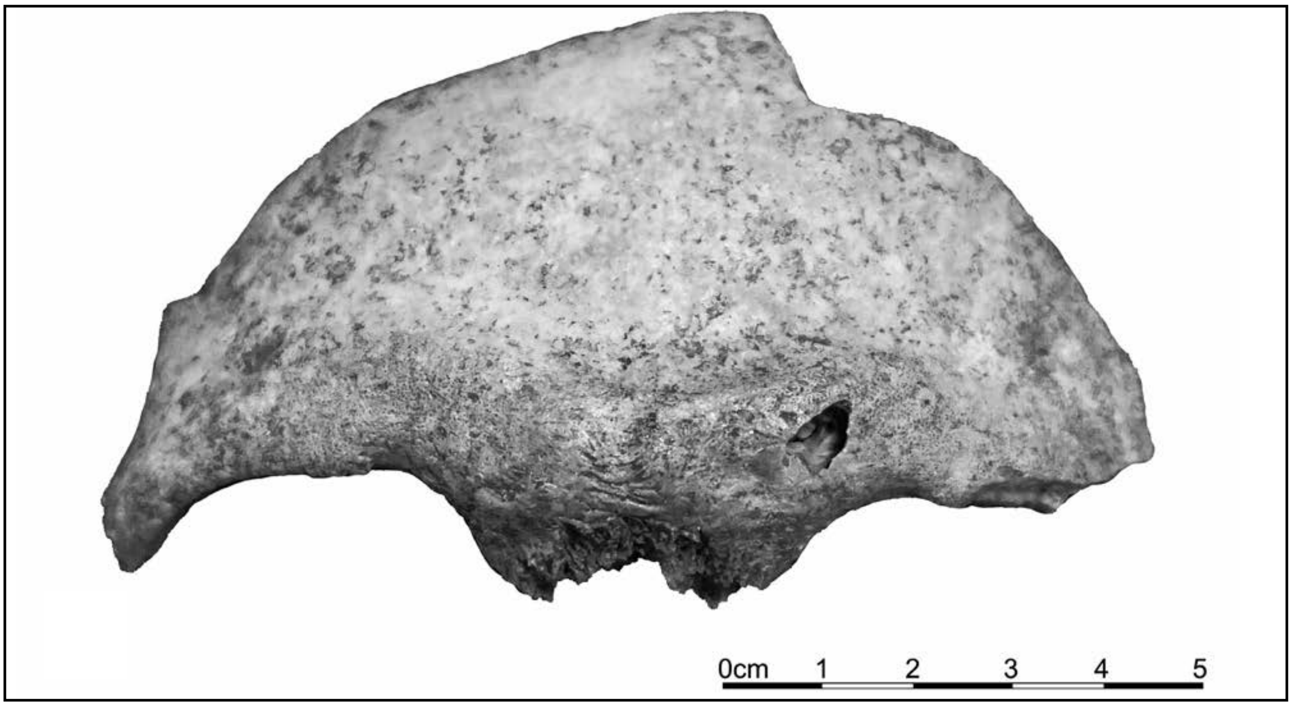


Figure 17. CWCHT RH-29. Human frontal from Robin Hood Cave. Frontal view.

Jenkinson (1984) observed that although Campbell (1977) assumed that all fragments belonged to the same individual, there is a significant difference in their state of preservation. The mandible shows signs of considerable root damage and generally has a darker brown coloration, making it appear as if it was found in a completely different part of the cave. The damage to the bone extends to missing part of the condylar and coronal processes, the angle has been worn into a very rounded shape, and the bone is broken off in close proximity to the mental foramen.

CWCHT:RH-28 Human temporal and sphenoid (Figure 16)

Two large fragments are part of the same bone and can be easily refitted along the fracture line to form a partial right temporal bone (see Figure 16). The first fragment consists of the petromastoid and tympanic parts of the temporal, while the second incorporates part of the squama and part of the greater wing of the sphenoid bone containing the foramen ovale. From one of the fragments is was possible to determine the sex of the individual, thanks to its large mastoid process indicating that the bones belonged to a probable male.

Both of these fragments were labelled as occipital bones and recorded as generic skull bones in the museum online database. A third, smaller fragment was catalogued as a generic skull fragment, yet it is in fact part of the greater wing of the sphenoid.

CWCHT:RH-29 Human frontal (Figure 17)

This partial frontal bone from Campbell's 1969 excavation, was determined to have belonged to a male individual, based on the prominence of the brow ridge and the thickness of the supraorbital margin. A large portion of the coronal suture is missing, additionally a puncture fracture is present above the right brow ridge (see Figure 17A). The lesion is stained on the inner surface and does not show signs of healing, hence it likely occurred when the bone was already exposed to the soil.

The bone was discovered in the OB layer in square D3 by the Western entrance to the cave (Campbell 1970; Campbell 1977). The fragment was later submitted for radiocarbon dating by Jacobi, and the results reported that the fragment sample OxA-7386 was of clear Early Neolithic origin, dating from 5000±40 BP (Hedges *et al.* 1998).

CWTCH:RH-30 Human cervical vertebra

As one of the few post-cranial bones discovered by Campbell in 1969, this third cervical vertebra is one of the human remains also reported by Jenkinson (1984). The bone is well preserved and in similar condition of colour to the previously examined fragments. This is consistent with the hypothesis that all the human remains unearthed in 1969 belong to the same individual.

Human lumbar vertebra (RH69 E-tip 68) and atlas

The specimens consist of a fully developed first lumbar vertebra and atlas (first cervical vertebra). Despite neither of the specimen being reported by Campbell (1977), it is suggested by the existence of a radiocarbon dating report that at least the lumbar vertebra was discovered as part of his 1969 excavation of Robin Hood Cave (Hedges *et al.* 1991).

There is no certainty to this claim however as that same report also contains incorrect information regarding the previously examined frontal RH-29 (Hedges *et al.* 1991).

The atlas is in a very good state of preservation with minimal damage to the left transverse process and the lumbar vertebra is missing parts of the left transverse process and the tip of the spinous process. The body of the vertebra shows signs of compression and of heavy corrosion, however, osteoporosis is excluded as a possible cause due to its healthy appearance. The lumbar vertebra was submitted for radiocarbon dating by Jacobi in 1988, and it was determined that the bone was of Neolithic age as were the other bones excavated in 1969. The sample, OxA-1807, was dated 4870±120 BP (Hedges *et al.* 1991, Charles and Jacobi 1994).

Human tibiae (Figure 18)
These fragments were recovered from an unknown location near, or within, Robin Hood Cave. Neither finder nor date are specified on the database. It is hypothesised that they were excavated as part of the 1969 Campbell excavation and reported as generic post-cranial bones. These are mentioned along with the discovered cranial remains, however, what specific bones were recovered is not reported (Hedges *et al.* 1991).

All fragments are heavy in weight and composed of hard compact bone unlike the other remains, which were all heavily decalcified. Of the three fragments, #79 is the largest and it was determined to be part of a left tibia. None of the fragments could be matched to the same bone, despite representing different sections of the diaphysis: #79 was determined to be part of the anterior border of the diaphysis, #150 is a fragment from the medial part of the bone, and #156 was identified as a section 3-5 cm above the distal epiphysis.

On one end of fragments #79 and #156 (in the areas indicated by circles on Figure 18) there are signs of damage which are likely to have been caused by animals gnawing on the bones. This is furthermore suggested by the longitudinal splintering and edge rounding.

Conclusion

Detailed descriptions of all the human material found in the Creswell Crags Museum and Heritage Centre (excluding that from the Whitwell Long Cairn) and Nottingham Natural History Museum, Wollaton Hall, collections, are provided here.

The detailed description of the material was often absent from previous papers, documents and museum records. These improved detailed records will simplify future recognition of the material by accurately describing their main features (colour, side, sex, approximate age at death, post-excavation treatments, etc.) and, non-metric variation. Signs of pathology and taphonomy have also been recorded such as the uneven dental wear of RH-24 and the gnaw marks on the unlabelled tibiae. In regard to dental pathology the majority of specimens presenting teeth showed signs of minimal to severe occlusal wear, however only RH-24 showed signs of calculus and FS4850 was the only one to have carious lesions. RH-24 also presented the Carabelli Cusp feature. Of

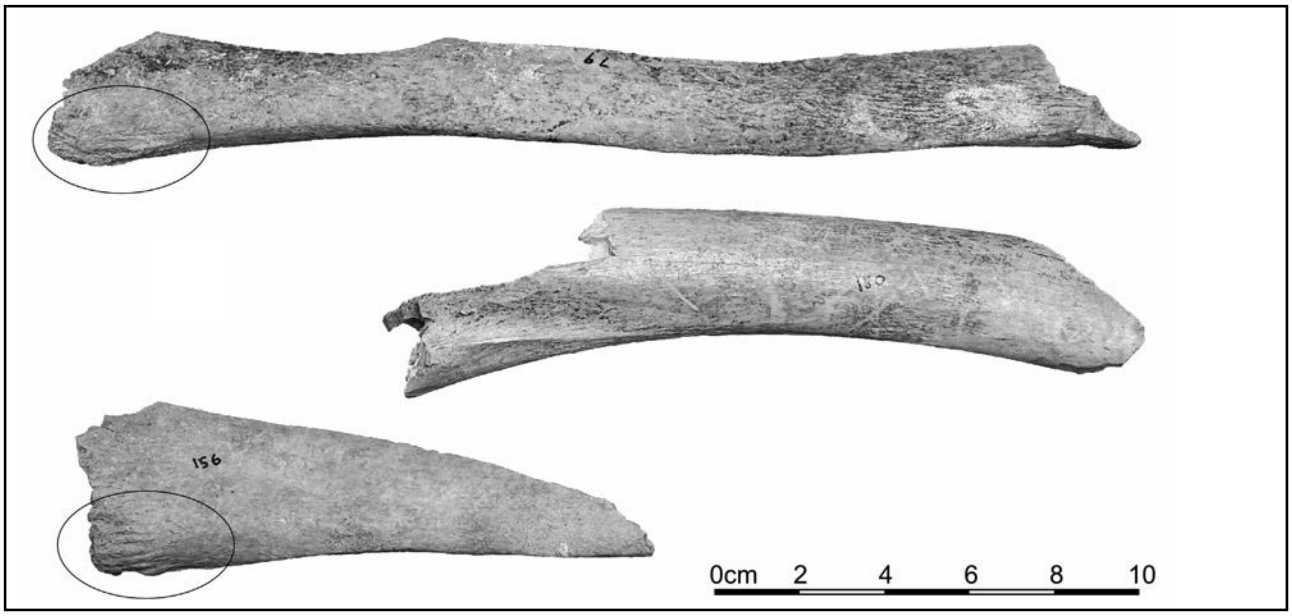


Figure 18. Fragments of human tibiae (#79, #150, #156) from Robin Hood Cave. External view of shafts showing fragment number and signs of possible taphonomic damage as indicated by the circled area.

the specimens aged using tooth wear, the likely more abrasive diets of the past, particularly in periods when quern-stones were being used, may overestimate the ages of the individuals. The chosen method by Brothwell (1981) for age determination from teeth takes these conditions into consideration and was developed specifically for prehistoric teeth; the method may be slightly less appropriate for Roman teeth.

Amendments were suggested for the label of specimen CWCHT:AT77, correctly listing the teeth present on the maxilla as reported above. Specimens such as CWCHT:RH-25 and CWCHT:RH-28 (excluding the small sphenoid fragment) now specify the exact bones represented by these fragments, leaving no doubt as to their identity. The vertebrae and tibial fragments present at CCMHC, which lacked museum accession numbers, have been linked to the material from the 1969 Campbell excavation. The project also grew to clarify some of the confusion and contradictions surrounding much of this material, including their ages and origins. With regard to the age of the material, radiocarbon dating information was recovered for three specimens from Creswell Crags, RH-23, RH-29 and the unlabelled lumbar vertebra, the first being from the late Iron Age/early Roman period and the other two being of Neolithic origin.

If possible, further research and information is required to clearly identify the provenance of the specimens held at the NOTNH. In particular, the age of the material from Colwick Hall could not be refined any further than the late Pleistocene/Holocene period based upon the information available at present. A skilled geologist or stratigrapher might be able to determine a more accurate date, however, the isinglass treatment may impact upon possible radiocarbon dating as it disrupts 14C testing and potentially provide a much younger age.

Acknowledgments

Many thanks to Fred Owen, Nottingham Trent University (NTU), for devising and supervising this study as my final year undergraduate project and for offering his knowledge of Creswell Crags, locating valuable literature and reviewing earlier drafts of this work. Dr Adam Smith from the Nottingham Natural History Museum, Wollaton Hall, is also gratefully acknowledged for facilitating access to the material studied and the museum records. Many thanks are also due to Ms. Lucy Astell at the Creswell Crags Museum and Heritage Centre for allowing full and free access to their collection and library.

Many thanks are also due to Dr. Christopher Terrell-Nield, NTU, for providing useful images and reviewing this paper, and to Dr. Rogan Jenkinson for offering his professional experience and notes from his time as past Director of the CCMHC and for answering my questions regarding the specimen.

My final thanks go to the reviewers who engaged with this research and provided useful commentary and recommendations on how to improve what was an undergraduate dissertation project, and turn it into a publishable paper.

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BOOK REVIEW

Writing for Science Students. **Jennifer Boyle and Scott Ramsay. Published by Palgrave, London, 2017. UK£14.99, paperback, xii+206 pages. ISBN 978-1-137-57151-9.**

'… you don't need to learn any new creative skill to become an excellent scientific writer' (p. 3).

When I was an undergraduate reading geology back in the late 1970s, books that helped students to master the academic writing process were rare, almost non-existent, or perhaps I just failed to browse in the right part of the bookstore. I do not think I discovered any at that time, although I started my library of writing references soon after, as a graduate student. Today, there is a plethora of writing guides for the undergraduate, lucky people, such the Palgrave Study Skills series to which *Writing for Science Students* belongs. The authors are confident in their approach to training the nascent scientific author - see quotation at the head of this review - but honing these creative skills still takes a reference book 200 pages in length. *Writing for Science Students* is aimed squarely at the undergraduate market. Masters theses get a mention, here and there, but this will tell the committed and well-informed research student little that they do not know already. Indeed, this is not a book aimed directly at readers of *The Geological Curator*, but for their students. Yet there is much in it that any scientific writer might consult as a 'dipper'. The book is dense, solid, not light reading by anyone's standards. So, in the eyes of some or many students, it may be just one more solid text rising between themselves and their degree like the Great Wall of China. Will undergraduates with poor writing skills want a 'quick fix' or will they commit to reading *Writing*? The book demands and deserves respect, but it may not be read by those that need it most. Yet the authors acknowledge that their book is more of a 'dipper' than a 'reader' (p. 54); that is, they expect students to pull out what they need rather than committing to reading the whole. So be it.

The first thing that jarred about *Writing* … was the common use of one-sentence paragraphs. The authors themselves recognize this to be a poor structure: '… very short paragraphs might point to a wider structural issue' (p. 140); 'A paragraph … should not be read as a random chunk of information' (p. 141); '… lots of small, disconnected paragraphs will ultimately have an impact on the overall coherence and structural tightness of the [document]' (pp. 143-144). A paragraph should be composed of two or more sentences that together explore a limited aspect within the focus of a manuscript. Paragraphs composed of one sentence are not common in academic articles; they are more typical of tabloid newspapers, which are commonly poorly written and unpleasant to read. That a book purporting to instruct in the methodology of academic writing should see fit to use this incongruous style is distressing. I counted seven one-sentence paragraphs in the first three chapters alone. Each of them would have been stronger if merged with a sequential paragraph discussing the same subject. As it is, they introduce an unsettling jerkiness to the text that decreases its effectiveness.

The authors subscribe to a general misconception in 'The Abstract' (Ch. 6). They lump together everything that academics refer to as an abstract, yet those in a 'scientific article' fulfil a very different purpose to that 'in a conference programme to advertise each presentation' (p. 46). That for any written article or report is a hook, informing the reader of the content of the main body of the text and, hopefully, drawing them in, encouraging them to read past the abstract. Thus, it is a prelude to a fuller report. In contrast, conference abstracts are preludes to ephemeral events, a poster or talk, but can only qualify as a hook beforehand. After the event, the conference abstract is the only record of a presentation that will survive for the information of those who missed the conference - what was it that X said in their talk? The two types of abstracts are thus dissimilar in function and should be written with different focuses. Each will serve future audiences in subtly different ways (Donovan 2017, pp. 39-41, 55-57).

The book emphasizes the IMRaD structure of scientific reporting - introduction, materials and methods, results and discussion - but seem too interested in following the results with conclusions about them rather than a discussion of them (p. 21). Discussion is the correct place to expound on the meaning and significance of results. I see conclusions as being a minor concern for writers of science. In truth, the abstract and conclusions are interchangeable - the abstract tells you what the document is about before you read it and the conclusion summarizes the same after you have read it.

I gained something from all parts of *Writing*, but 'Incorporating and Referencing Other People's Work' (Ch. 8) was particularly stimulating, explaining for students how to avoid plagiarism and write with your own voice. I have a slight quibble with the section on 'Commonly used referencing terms and their meanings', which considers that quoting is 'Not often used in science' (p. 73). Maybe, but the examples used throughout this book come from physics, chemistry and biology, whereas I am a geologist and palaeontologist, two fields to which *Writing* … pays little attention. My interests are historical sciences and rely, at least in part, on history. I am no stranger to using relevant quotations in my papers, but Boyle and Ramsay are strongly against their use in other areas of science. We will have to agree to disagree.

It was interesting to read that '… journal articles are typically very short - usually fewer than ten pages' (p. 80). Again, this may be a cultural contrast between sciences. Although I, personally, write many short papers, my impression is that there is a preference for geologists to publish longer papers, driven by promotion review boards and grant authorities. (Obvious exceptions are leading journals such as *Nature* and *Geology* which only publish brief papers.) While I note a move away from certain traditional short publication forms in at least some geological journals, such as book reviews and 'Letters to the Editor', perhaps this is not the case in chemistry and elsewhere. An informed survey of these trends would make interesting reading.

I offer my strongest congratulations to the authors for figures 9.4 and 9.5, and the simple, yet most important labels: 'Caption text fully explains data'. Hooray! So often, writers of science, from the humblest student to the most senior academic, neglect the simple, yet essential art of writing informative figure captions. A figure and its caption should be able to stand alone as a piece of scientific research without the crutch of the associated text. If you can do that, you will communicate science in the best way possible. Yet this good example stumbles in figure 9.7, 'Use of colours in a figure', yet printed in black and white! Surely this was the unhappy fault of the publisher.

I can only support Boyle and Ramsay as they try hard to engrain the message that nobody should write the final version of a document without prior drafts (Ch. 11, 'Producing a Draft and Building Your Argument'). Unfortunately, my own experiences suggest many or most students see multiple drafts as a waste of time, but they are horribly wrong. In the early 1990s at the University of the West Indies in Kingston, I instigated a change in the number of drafts, from one to two, which it was compulsory to submit to the supervisor of a final year undergraduate project. Anyone who failed to submit both drafts automatically failed the course. This rigid system worked: there were fewer failures and, overall, standards were raised. If only Boyle and Ramsay could apply their edicts in such a draconian manner.

Boyle and Ramsay suggest that undergraduates should devote blocks of '… a couple of hours' at a time to writing (p. 133), but also note that '… 10 or 15-minute blocks [distributed] throughout the day, can be an effective way go get a surprising amount of writing done' (p. 134). They also look at environment - where are you most productive? Be there! I can only agree with much of this chapter. For example, I wrote the first 700+ words of this review in brief bursts on stick'n™ notes and stuck them to the relevant pages in *Writing*. I typed these up and left the review to lie fallow for a few days. I then blitzed the ending today, writing over a twelve hundred words at home, and at two favourite cafes for breakfast and lunch. Mix, match and make it work.

Some minor errors of fact have crept in. For example, a Ph.D. is not the highest degree a university can award (p. 68) - what of a D.Sc.? Was the central dogma of molecular biology really '… each gene has instructions for making one protein' (p. 112)? I am not sure that Francis Crick would have agreed (Olby 2009, fig. 13.2). Other small errors crept in, probably at the proof stage. Thus, '… prevent them from happening them' (p. 164) makes no more sense than '… changes how you to interpret' (p. 179). Yet there is one most effective piece of poor typesetting (p. 186):
'… cause your grade
to drop.'

The authors emphasize the importance of reference lists being well-organized and consistently formatted (p. 42), yet their own bibliography is anything but (pp. 201-202). Oh, dear. Places of publication and publishers are listed in various styles, such as 'Harper Voyager, London', 'New York: David McKay Company' and 'Jones & Bartlett Learning (s.l.)'. Pitkin et al. was published in the journal *JAMA* (italicized), but Pitkin and Branagan appeared in JAMA (not italicized). And so on. These are the sorts of booby errors that I expect in student essays, where I would have red inked them, and send them back for correction and a little more thought. Finding them in a book of this sort is disconcerting and will hardly be a good example for the budding student author.

In conclusion, this is a book more for your students than for you. Should your undergraduates read and use *Writing for Science Students*? Yes, indeed. It will be to your benefit (as marker) as well as theirs, but do ensure that they do more with it than admire the spine on their bookshelf. It is a book that will repay being read, not admired from a distance. I also emphasise that there is much in it to refresh the memory of even an experienced author - a copy on your own shelf might be a useful prompt when you ask yourself 'how should I write that?'

References

DONOVAN, S.K. 2017. *Writing for Earth Scientists: 52 Lessons in Academic Publishing*. Wiley-Blackwell, Chichester, xv+227 pp.

OLBY, R. 2009. *Francis Crick: Hunter of Life's Secrets*. Cold Spring Harbor Laboratory Press, Cold Spring Harbor, New York, xix+538 pp.

Stephen K. Donovan, Naturalis Biodiversity Center, Leiden, the Netherlands

JOY IRVING (1951 - 2019)

It is with great sadness that we report the death of Joy Irving. She joined the staff of the Oxford University Museum of Natural History in 1991, working as a technician across Geological and Mineral Collections. Joy brought enthusiasm and friendliness, together with three invaluable attributes for museum work: beautifully neat handwriting, meticulous attention to detail, and a good grounding in her specialist subject - geology.

Born in Holbeach, Lincolnshire, Joy acquired her love of sciences, especially chemistry, while at Spalding High School. She was studying for an Open University Degree when her husband's work took them first to Papua New Guinea and later to live in Namibia. Ever intrepid explorers, they took to desert roads to see the massive dunes, rock carvings and paintings with first one and then two young children. Joy loved hunting for semi-precious stones in the gravelly desert floor, and the peace of the Namib desert at night. It was in Namibia, she completed her studies, nursing her young daughter on her knee. In a country of great mineral wealth, her interest grew, and she went on to take a Masters degree in Mining Geology at the University of Leicester. Originally her intention was to work abroad but opportunities were rare indeed for female geologists, and so the mining industry's loss was to become the museum sector's gain.

In the Museum, as well as keeping mineral cataloguing up to date and identifying and cataloguing the

Carboniferous plant collection, Joy worked on displays, at public events, and on the multitude of other tasks that came her way. A large part of her time was spent dealing with the conservation of pyrite and marcasite-bearing minerals and fossils, carrying out detailed condition reports as she set up microclimate storage, first using silica gel and then moving on to anoxic storage. She queried, experimented, and modified procedures to optimise the care of these vulnerable specimens. It is a massive credit to Joy that throughout her long tussle with cancer, she was back in the Museum whenever she could be, working on the pyrite conservation programme. Even after she retired in 2010, Joy returned week after week to maintain the microenvironments that would keep some of our most sensitive specimens in good condition. She spoke at professional meetings and published on pyrite preservation, and her final joint paper is published here.

We'll remember Joy for her kindness, her great sense of fun and for her love of bright colours. In her private life, Joy was a free spirit, adventurous and creative, and passionate about the environment and about her own family. Our condolences go to her husband Bob, their son Rupert, daughter Tamsin, and grandson Manué.

Monica Price and Juliet Hay, 10 June 2019

THE GEOLOGICAL CURATOR

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4. Single space-bar between words, **double space-bar between sentences**.
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