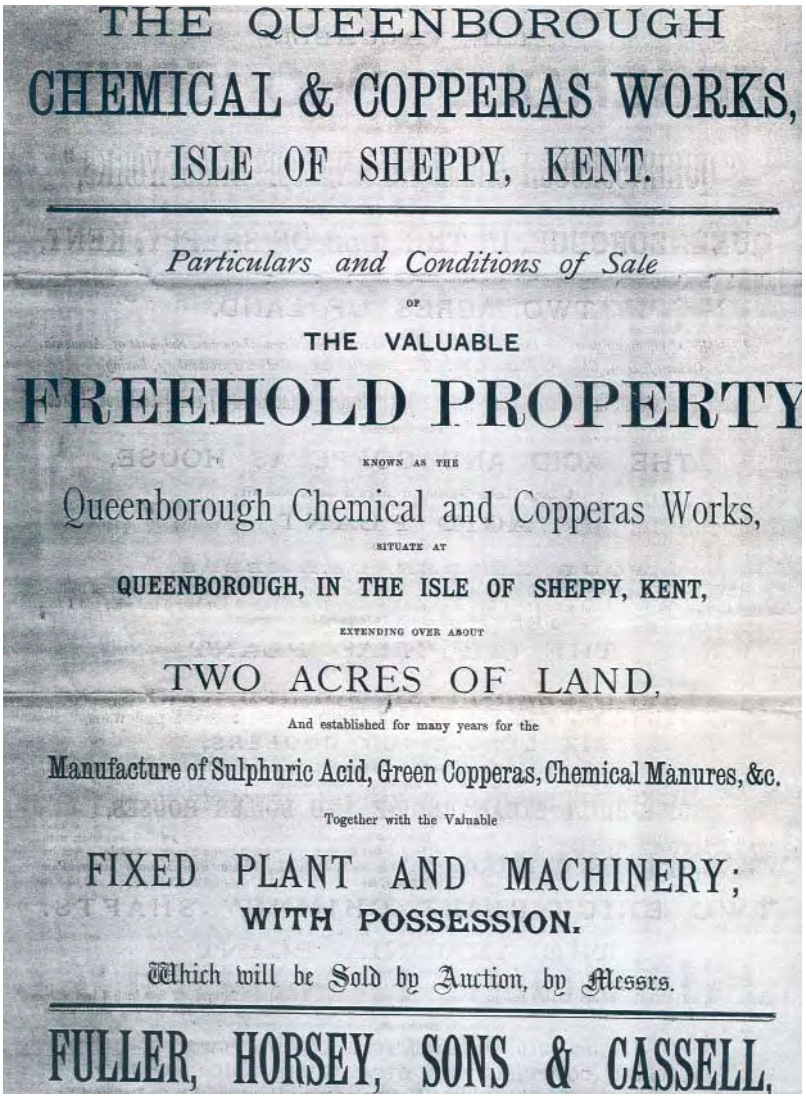
The trouble with Pyrite

By Fred Clouter

On Wednesday the 26th April 1882 the Queenborough Chemical and Copperas Works were auctioned off, heralding the demise of the copperas industry on the Isle of Sheppey. Green copperas was used to make sulphuric acid or vitriol, chemical manures and dye stuffs.



THE QUEENBOROUGH

CHEMICAL & COPPERAS WORKS,

ISLE OF SHEPPY, KENT.

Particulars and Conditions of Sale

OF

THE VALUABLE

FREEHOLD PROPERTY

KNOWN AS THE

Queenborough Chemical and Copperas Works,

SITUATE AT

QUEENBOROUGH, IN THE ISLE OF SHEPPY, KENT,

EXTENDING OVER ABOUT

TWO ACRES OF LAND,

And established for many years for the

Manufacture of Sulphuric Acid, Green Copperas, Chemical Manures, &c.

Together with the Valuable

FIXED PLANT AND MACHINERY;

WITH POSSESSION.

Which will be Sold by Auction, by Messrs.

FULLER, HORSEY, SONS & CASSELL,

'Being in Queenborough Castle in the year 1579 I found there one Mathias Falconer, A Brabander, who did in a furnace that he had erected there, trie to drawe very goode brimstone and copperas oute of a certain stone that is gathered in great plenty upon the shoure near untoe Minster on the isle' This extract is from 'Lambard's Perambulations of Kent' and is probably the earliest known reference to a 'chemical' factory in Britain.

The first reference that I have that links copperas with the collection of fossils is found in the 'Life and letters of Edward Lhwyd (second Keeper of the MUSEUM ASHMOLEANUM) Oxford March 28th. 1695'. Below is an excerpt from
'A Museum of the Early seventeenth Century'
By Cyril Edward Nowill Bromhead, BA, FGS, FRGS. (Read 18Th. June, 1947) referring to the Lhwyd letter

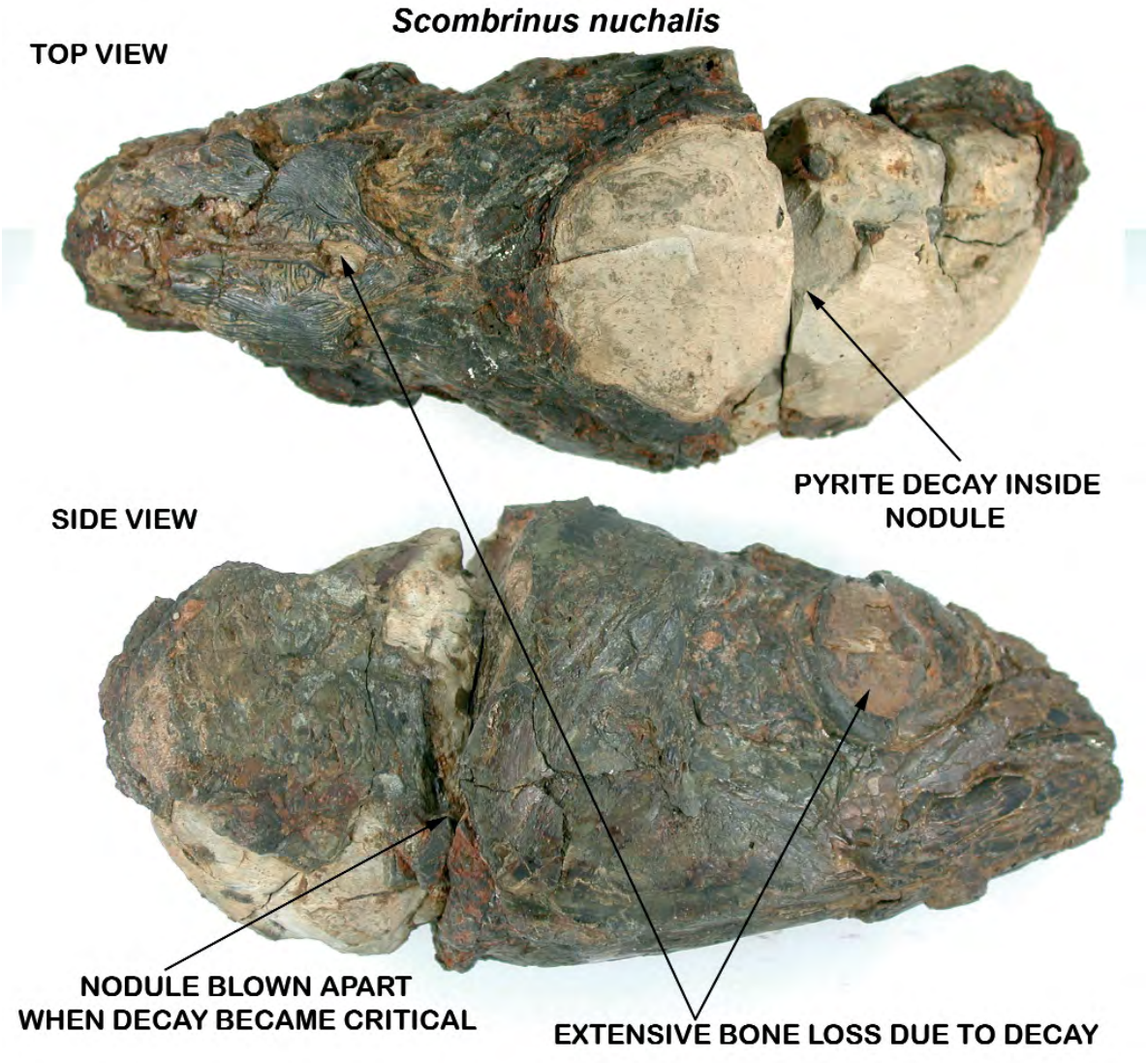
(If you could setle a correspondent in the Isle of Shepey to save us all the Crampstones the copras-women pick up for a month or two, I would now fall about a Lithologia Britannica: and so contrive it that the first tome shall consist of onely teeth and bones of fish.)

(Shark teeth were called cramp stones as they were ground up and used as a remedy for stomach complaints)

Copperas as you will no doubt have gathered is just another word for pyrite (iron disulphide, FeS2). The form found on Sheppey is marcasite (iron disulphide, FeS2) and is dull green in colour when fresh, quickly deteriorating to a rusty brown when exposed on the beach for some time. Chemically identical, pyrite and marcasite are very different in behaviour. The normal gold coloured pyrite has dense molecules and tends to be more stable than the more open molecules of the marcasite stones. Fossils preserved either as pyrite casts, or containing pyrite within bone are prone to pyrite decay. Many different methods have been tried by collectors to preserve pyrite specimens over the years, all with very little long term success.

There is nothing more depressing to the fossil collector, or the museum curator who, when inspecting prized or unique specimens finds a little heap of whitish dust, an eroded data label

and a discoloured box; even wooden cabinets can be severely damaged. It may be a few months, or a few years of exposure to the air, but the inevitable decomposition will take place. The chief oxidisation products are sulphuric acid and various hydrated sulphates, mainly iron. The acid will also destroy associated shell and bone material. It is now generally accepted that the decaying process is caused by a form of oxidisation and is triggered by exposure to humidity in the atmosphere. It seems that the fossils absorb moisture from the air which reacts with the pyrite and the air. In tests under humid conditions the reactions can be catastrophic. However if the water vapour is removed the reactions are slowed down and can eventually stop. The more compact forms of pyrite do not absorb moisture so readily and may only evidence decay by surface tarnishing. Various methods have been tried over the years, both by museums and individuals to stop the decay. Most have been unsuccessful. I do not believe that there is a method that can guarantee complete success but I do think that with effort the process can be slowed down. In the following paragraphs I shall attempt to describe some of the methods that I have tried with varying degrees of success.



Before treatment it is important to thoroughly wash all contaminants such as clay and salts from the specimen. Salt is taken up by the specimen if it has been washed over by the tide. Wash the specimen with clean water, some wash their specimens with boiled or distilled water, but this is purely personal choice. Change the water every day. The specimen should then be dried, but do not dry the specimen artificially as this can damage fragile specimens. Have a plentiful supply of self seal plastic wallets, or plastic jewellery boxes of various sizes. It is very important that specimens are kept separate. One decaying specimen will infect others if in contact. Store your specimens in a dry atmosphere, damp outbuildings or sheds are totally unsuitable.

The chemicals used by museums are not discussed here because I don't know how to use them. If interested it is claimed that the use of Ethanolamine Thioglycollate has had some success treating decaying pyritised fossils. It is also claimed to be effective as a reagent for the removal of pyrite oxidisation products. I have not had access to this chemical so cannot comment.

Pyrite accumulations on the beach near to Barrows Brook, Isle of Sheppey, North Kent

When I first began collecting on Sheppey I avoided pyrite fossils, only collecting the larger phosphatic and calcareous ones. I then discovered Folkestone and the beautifully preserved but pyretic ammonites to be found there. Preservation became a real issue as some of the older beach collected specimens had been washed over by the sea. Because the pyrite is porous, salts had been deposited at a molecular level within the specimen. This is why washing thoroughly is so important. If the nacreous shell of the specimen is still present, the problem is, how to A, preserve the shell, and B, treat the pyrite.

Method 1. For Gault ammonites only

The shell looks fabulous when wet, but always appears whitish and powdery when dry, often falling away from the internal cast. The Folkestone ammonites need to be washed very carefully with a soft brush under softly running water to remove any remaining clay. When dry coat the shell, one side at a time with 'Sally Hanson' 'Hard as Nails' varnish. This is reinforced with nylon which helps to stabilise the shell. Allow to dry and then place the specimen in a bowl of liquid paraffin. Almost by magic over a day or two, the shell will be transformed from a creamy white to a beautiful iridescent pearly colour caused by the paraffin contained by the nylon. I have many excellent specimens up to 15 years old which show no signs of deterioration. This method works only to enhance the nacreous shell and is not useful for preserving other fossils.

Method 2.

This method is more generally useful and can be used for fossils from Sheppey or Folkestone and I would expect fossils from other locations. This is my 'Heath Robinson' method, which I

have been using since 1995 with mixed success. It has proved very useful for most types of pyrite fossils, but not the little seeds and carbonaceous fossils from Sheppey. (I will explain why a little further on.) My reasoning was very simple, keep the moisture away from the fossils and try to treat it at a molecular level. I searched around for a substance which could do this. I came across 'Ronseal wet rot wood hardener', a gooey resinous liquid which was thinned with acetone. Very simply, after washing, the specimens were immersed in a 20% solution which soaked through the fossil. If possible a vacuum environment will drive the liquid further in to the specimen however I didn't have one so they just stayed soaking for about a week. If the specimen came out of the solution and appeared shiny the solution was to strong so the whole process was repeated with a weaker solution. Hit and miss you might think, but not one of my little bivalves or gastropods from Sheppey have decayed in more than ten years. If used on Folkestone ammonites the shell is hardened, but the colour stays a more natural tone than the preceding method.

The woody seeds and twigs from Sheppey are very difficult to preserve. They are a mixture of carbonaceous material and pyrite and when drying the woody material shrinks while the pyrite stays the same. Consequentially the woody material flakes off as soon as drying begins. I have never successfully maintained the stability of these fossils using these methods. The Nippa palm fruit is notoriously prone to decay. I have managed to delay decay up to a couple of years by soaking the Nippa in the Ronseal liquid while it is still wet. The resins that it is made from tend to repel moisture and the acetone evaporates very quickly. When set, immediately immerse in a fairly strong solution of PVA which dries to give a flexible coating helping to stabilise the carbonaceous material. I think that making a mould and casting in acrylic resin to make a replica is the best way of keeping a reference to the seeds and woody fossils. The important thing is to keep your pyrite fossils dry, below 50% humidity. Tiny seeds can be kept in sealed containers with silica gel. As long as the silica is changed before it gets too damp the fossils may survive longer.

Nippa husk suffering from pyrite decay

Method 3

This method is essentially the same in principle as method 2 except that Paraloid is used in place of the Ronseal. Paraloid comes in the form of little plastic granules which are soluble in acetone. It can be mixed as a thin solution or as thick glue. It is clear when dry. Fossils can be immersed in the same way as with the Ronseal and it will coat the fossils at a molecular level if thin enough. It will take a little trial and error to get the consistency right. I am told that the NHM uses Paraloid in their conservation department. It is useful for many conservation purposes beside the treatment of pyrite.

(Both the above treatments are reversible by soaking in neat acetone. PVA is not suitable for use in the treatment of pyrite. Commercial products may contain other chemicals which may be harmful to the fossil.)

Brychetus meulleri successfully treated for pyrite decay using the Ammonia vapour technique

What to do if your specimen begins to show signs of decay

If you catch it early enough it may be possible to arrest the deterioration. The white powdery substance is very acidic and will need to be neutralised. Some rather odd techniques have been recommended in the past which involved using various disinfectants reputedly destroying the 'bacteria' and so preventing decay. I have never tested these methods so cannot say how effective they are. The method that I use involves using a strong solution of Ammonia, a very dangerous liquid so it is only recommended if you are experienced using chemicals of this kind. The idea is not a new one and I am sure that more modern techniques are less dangerous and probably more effective but I don't have access to these more scientific methods. Simply put, the ammonia converts Ferrous Sulphides to Ferrous Oxides (rust) which is much less harmful to the specimen. It does not help if the specimen is too far gone; it will most likely end up as a small heap in the jar. The specimen must be exposed to an atmosphere of 80% ammonia for several days. Do not under any circumstances immerse the specimen in the ammonia solution. The specimen must be exposed only to the fumes. The specimen will eventually turn a warm rust colour. This is not ideal, but is much better than losing the specimen. Then treat the specimen in one of the methods outlined in the previous paragraphs. Remember to isolate your pyrite fossils in either sealable plastic wallets or in individual plastic boxes.
It is of the utmost importance that the ammonia chamber is sealed; otherwise the ammonia atmosphere will dilute in the air and be ineffective. For very small specimens I use a coffee jar with a glass lid which has a plastic seal, easily acquired from any supermarket and is ideal for the job. A small glass phial containing the Ammonia is placed with the specimen and left for a few

days. For larger specimens like fish skulls with pyrite within the bone structure I have used a bell jar sealed with petroleum jelly and for very large specimens a square plastic storage bin placed on glass and again sealed with petroleum jelly. The latter, a very large fish skull (Brychetus meulleri) 30cm by 35cm needed to be exposed to the ammonia for over two months but has remained stable since the treatment was completed five years ago.

I am not a conservator or a scientist so the more technical papers that I have read to do with Pyrite conservation have only been partially understood by me. However I have had some measure of success, fingers crossed, not losing any of my specimens except for some of the more woody and seed material to the dreaded disease since I began collecting in 1995. If you are advised by the well meaning to embed your specimen in clear casting resin, or to brush your specimens with hot clear candle wax or paraffin wax as has been suggested to me in the past, don't pay any attention to them, they won't work. The only sure ways to record for posterity your unique or important specimen is to either make a cast of it or to photograph it so that if the worst does happen as it is more than probable that it will, evidence of the specimen will not be lost for future generations.

References

Some tips on preserving pyritised fossils, Jim Craig 1978
Pyrite conservation part 1 historical aspects F. M. P. Howie, Newsletter of the Geological curators group No9 April 1977
Pyrite conservation part 2 F. M. P. Howie, Newsletter of the Geological curators group No10 Sept. 1977
Museum climatology and conservation of Palaeontological material, F. M. P. Howie,
Special papers in palaeontology 22 1979
Use of Ethanolamine Thioglycollate in the conservation of pyritised fossils,
Lorraine Cornish and Adrian Doyle, Palaeontology Vol 27 pt 2 1984
Conservation of your geological collection
Seminar notes AMSSEE travelling geology curator, Simon Timberlake 1988
An experimental Ammonia gas treatment method for oxidised pyretic mineral specimens,
ICOM committee for conservation 1987 working group 15, Robert Waller
Ronseal technical safety data sheet for Ronseal wet rot wood hardener 2002
A Museum of the Early seventeenth Century' By Cyril Edward Nowill Bromhead, BA, FGS, FRGS. (Read 18Th. June, 1947)
Early Science in Oxford by R. T. Gunther vol XIV

Some useful web addresses

Pyrite conservation -
http://www.nhm.ac.uk/research-curation/science-facilities/palaeo-conservation-unit/amd/amd.html
http://www.discoveret.org/kgms/feb-01/feb01-8.htm

Fossil preparation and conservation -
http://www.flmnh.ufl.edu/natsci/vertpaleo/resources/prep.htm
http://www.mineralogie.uni-wuerzburg.de/palbot/tools/preparation.html

Paraloid supplies -
http://www.conservation-by-design.co.uk/sundries/sundries20.html
http://www.archivalaids.co.uk/smx/products/paraloid/
http://www.sylmasta.com/acatalog/Powders___Chemicals.html

Acetone - http://www.mistralni.co.uk/products.php?type=solvent
http://www.shellchemicals.com/acetone/1,1098,806,00.html