

Conservation of pyrite damaged ammonite type specimens at the National Museum of Wales



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Abstract

A project to conserve, cast and repackage a collection of Jurassic ammonites from Dorset was undertaken at Amgueddfa Cymru - National Museum Wales. The specimens are all either cited or figured and include holotypes and paratypes. Many had been consolidated 40 years ago with the acrylic resin Bedacryl and some were embedded in plaster. The Bedacryl had become tacky with age and dust that had settled on it was difficult to remove. Pyrite is present in the rock and the fossils and many of the ammonites were affected by pyrite decay. The specimens were cleaned, treated for pyrite decay if required, re-consolidated and packaged in protective microclimates. Due to the scientific importance of the collection, casts were made of some of the ammonites to ensure a good record of the specimens, in case of further deterioration of the original specimens. Following re-consolidation, silicone moulds were taken of the specimens and from these, casts were made. It was important that the casts should be free of even microscopic bubbles, and after some experimentation it was found that the addition of the antifoaming agent Simecicone significantly reduced the number of bubbles in the casts.

Keywords: Pyrite Decay; Ammonite; Microclimate; Conservation; Casts.

Introduction

The Department of Geology at the National Museum of Wales (NMW) houses a collection of fossil ammonites from the Jurassic of Dorset. It includes approximately 160 specimens, many of the genus *Pectinatites*, collected during the 1960s and 1970s by J.C.W. Cope (Cope, 1967; 1978). The specimens are stored in the type fossil collection at the National Museum of Wales, Cardiff. The store is air conditioned and the temperature and relative humidity (RH) are within the ranges of 20-25°C and 40-60%, respectively.

Many of the specimens are naturally crushed, although the ribbing is generally well preserved. The rock is very fissile and has the mineral pyrite (Buttler 1994; Larkin 2011) finely disseminated throughout. As a result, and due to some of the pyrite oxidising, most specimens are extremely fragile (Figs. 1 and 2). The rib interspaces are often filled with hard shale, and often the entire specimen was originally encrusted with irregular pyrite aggregates (Cope, 1967). This presented considerable challenges during the original preparation of the specimens.

Many of the specimens were set in plaster at the time of collection in order to stabilise and extract them in one piece. Following original preparation in the 1960s, the specimens had been treated with ICI Bedacryl, both to consolidate the ammonites and to delay pyrite oxidation through the formation of a barrier for oxygen and water vapour (e.g. Howie, 1978).

Bedacryl is a hard, transparent, glass-like and thermoplastic polymethacrylate (PMM) resin. PMM resins were commonly used as conservation consolidants in art, archaeology and palaeontology during the 1950s by being applied directly to a specimen to prevent contact of its surface with air (eg. Costagliola, *et al.*, 1997). Resin coatings have been shown more recently to be an ineffective method. Some may provide a limited barrier against gases and humidity by decreasing a specimen's natural porosity (Costagliola *et al.*, 1997) but most are not impermeable to gases and humidity (Cornish & Doyle, 1984).



Fig. 1. One of the specimens, an ammonite of the species *Pectinatites (Arkellites) hudlestoni* prior to treatment (NMW 77.12G.528). Damage from pyrite oxidation products shows as bright areas. The plaster jacket is just visible around the edges of the specimen.

Bedacryl fell into disuse during the 1970s when the toxicity of the solvents used with them (toluene, xylene) restricted their wider use. In addition, sealing specimens with resins inhibits analytical processes or further conservation measures and is therefore not recommended (Buttler, 1994).

Following 40 years of storage, the Bedacryl coating on the ammonites at NMW had disintegrated and become tacky. Unfortunately this meant that 40 year's worth of dust settling on the specimens was very difficult to remove. A more threatening problem was that the specimens had only been coated on one side, oxygen and water vapour had been able to pass through from the other side uninhibited. Pyrite decay now appeared to be progressing, threatening to destroy the specimens. It was therefore decided to treat the ammonites for pyrite decay, following a procedure described in detail by Waller (1987). This method attempts to delay destruction of the specimens by neutralising pyrite oxidation products through exposure to ammonia gas.

Preparation

A prerequisite for the effective treatment of pyrite decay was the removal of the consolidant to enhance penetration of the ammonia gas; this would also serve to clean the specimen surface. The specimens were therefore immersed entirely in a bath of acetone for up to several hours. Acetone did not dissolve the Bedacryl, but it softened the old consolidant and separated it from the fossils; gel-like sheets became detached and were removed gently with a soft brush. Additional gentle rinsing with acetone achieved near-complete removal of the Bedacryl. Once the old consolidant had been removed the specimens were very fragile and needed to be handled with extreme caution.

At this stage, it was possible to undertake additional preparation of the specimens to remove any adhering rock fragments that had not been removed during the original preparation, as well as remove plaster from the original stabilisation, that



Fig. 2. Damage from pyrite decay to one of the specimens (*Pectinatites reisiformis*, NMW 77.12G.485); pyrite decay products are visible as yellow-white powdery substance.

was obscuring the specimens. This was undertaken using a Model ST fossil preparation pen (from Ken Mannion, Barton upon Humber) and a Model AJ-1 air abrasive machine (Texas Airsonics) with sodium bicarbonate 50 μ m powder. This preparation had to be undertaken with extreme caution in order not to result in physical damage to the specimens.

Pyrite treatment

Pyrite can oxidise in the presence of water vapour and oxygen, forming, for example, sulphuric acid and ferrous sulphate (eg. Newman, 1998). Sulphuric acid is a strong electrolyte, which can lead to oxidation of further minerals present in the fossil; ferrous sulphate exists as any of three hydrates, with each transition being associated with a volume expansion, leading to further physical specimen damage.

The standard method for pyrite treatment subjects specimens to ammonia gas, which neutralises the products of pyrite oxidation (eg. Waller, 1987). The specimens were exposed to ammonia gas in a desiccator for several hours and up to a few days, depending on the size of the specimens. A humectant (polyethylene glycol (PEG) 400) was added to lower water vapour pressure during the neutralization reaction. This results in less water condensation in fractures within the specimen. The length of treatment was determined by a reaction indicator. The depth and speed of the neutralisation reaction is dependent on a number of factors, such as specimen size and permeability, and amount of oxidation products. An indication of the probable depth of the reaction can be gained by inclusion of a small glass tube, packed to the depth of the specimen with a reactive sulphate mixed with small glass beads. Ferric sulphate shows a clear colour contrast between non-reacted (green) and oxidised (yellow-brown) material. Following the ammonia gas treatment, the specimens were stored in sealed containers with relative humidity kept low by the addition of silica gel until re-consolidation and packaging was completed.

Consolidation

Re-consolidation was undertaken to strengthen the specimens as they were extremely fragile following removal of the previous consolidant. A consolidant should have long-term stability, short-term reversibility and ease of application. The solvent used with the consolidant in this case was selected on the basis of vapour pressure, as a high vapour pressure allows the consolidant solution to dry within a short time so that several applications could be undertaken in short succession. This is not always the case; in some applications the depth of penetration is more important, in which case a solvent with a lower vapour pressure (such as ethanol) would be used. A solution of Paraloid B72 in acetone has been used in geological specimen preparation and conservation for many years with no apparent problems. Therefore the specimens were submerged completely in a weak (5 %) solution of B72 in acetone. Then loose parts were re-attached using HMG Paraloid B72 adhesive, taking care not to over-apply the consolidant or glue and obscure any morphologically important detail. Finally, a weak solution of the consolidant was injected repeatedly into any fractures using a syringe and hypodermic needle or a plastic disposable pipette (Fig. 3).

Casting

Following the neutralization treatment and consolidation, positive casts were made of the important type specimens. This ensured that at least replicas would be available for future study, should it not be possible to slow down the rate of pyrite oxidation sufficiently to preserve the specimens for future use and the specimens were damaged by the oxidation products. This was undertaken immediately after consolidation while the specimens were in a reasonable state of preservation, as well as newly consolidated and relatively stable, and prior to packaging in barrier film bags. Moulds were prepared using silicone rubber (Silastic 3498; Thomson Bros, Newcastle upon Tyne) which was selected to have a low viscosity for faithful replication, as the ammonites were of complex shapes and contained fine morphologically important details. The silicone rubber had to be flexible and separate easily from the fossil without tearing but also without adhering to the specimen too strongly and damaging the fossil during demoulding. Initially, white silicone rubber was used but it is advisable, should there be any need for future photography, to add a black or dark grey dye during mixing.

Jesmonite was used to make the casts. This is a gypsum-based casting medium in an acrylic resin. This product is relatively cost-effective, durable and has good long-term stability. It was prepared as suggested by the manufacturer: mixing an amount large enough to allow the stirrer (a paddle attached to a drill) to be fully immersed without dragging air into the mixture. However, on closer inspection of the casts under a microscope it was found that the casts contained a large number of small (barely visible with the naked eye) bubbles. Due to the



Fig. 3. Ammonite after completed treatment (*Pectinatites reisiformis*, NMW 77.12G.410).

scientific importance of the specimens this was unacceptable, and different techniques were tried to reduce the incidence of micro bubbles. Attempts included different mixing ratios of Jesmonite powder and resin, casting under vacuum conditions, and placing the moulds on top of an ultrasonic water bath immediately after pouring the Jesmonite.

Finally, it was discovered that the addition of an antifoaming agent gave much better results. The author's daughter had not long been born, and his wife observed the dispersion of washing up liquid bubbles when washing an empty bottle of Infacol ('formulated to relieve wind, infant colic and griping pain'). She therefore suggested trying the addition of a few drops of Infacol, readily available in any baby-bearing household, to the casting mix. Infacol is effective by dispersing bubbles, and it was hypothesised that it may have the same effect in the casting mix as in a baby's stomach. This worked remarkably well but greatly reduced the working time, as it accelerated the setting of Jesmonite to a few minutes. Advice from the manufacturer led to the further addition to the casting mix of a retarder, which then gave the desired results and very faithful casts. The active ingredient in Infacol is Simeicone, which can be obtained from laboratory suppliers. As Infacol also includes a number of other ingredients, it was decided to continue further experimentation with Simeicone alone to keep the number of chemicals added to the casting mix to a minimum for reasons of long-term stability. Approximately 1 drop of Simeicone was added to each 100g of Jesmonite.

The resulting casts and the moulds are now stored separately from the type specimens. The silicone rubber moulds have a shelf life and become brittle after approximately ten years (partly depending on how often they are used for casting). However, the casts can be treated as master casts from which further moulds and casts can be reproduced should this be required, for example for other museums or researchers. These master casts will be available long-term should the original specimens deteriorate further in the future.

Re-packaging

Complete sealing from the ingress of oxygen and water vapour with resins is unachievable, as even modern consolidants are permeable to some extent (Buttler, 1994; Larkin, 2011). In order for the treated specimens to be stored again in NMW's fossil store, without risking continued rapid pyrite oxidation and hence ineffectiveness of the treatment just undertaken, the treated specimens were packaged in individual microclimates. This involved sealing the specimen with an oxygen scavenger and/or a desiccant in a purpose-made bag using barrier film (Buttler, 2006). The barrier film used was Escal, a ceramic deposited barrier film with a polypropylene outer layer, a barrier layer of a vacuum-deposited ceramic on a PVA substrate and an inner (sealing) layer of polyethylene (Fig. 4). Barrier films were originally developed for the food industry, and oxygen scavengers for the electronics industry, to overcome similar problems of storing objects at certain relative humidity and oxygen levels. For the ammonites, two types of microclimate were used: the majority of specimens (those that had little or no obvious pyrite present) were stored in low RH microclimates of Escal barrier film with silica gel, and some (those with considerable pyrite-related damage) were stored in anoxic microclimates using two layers of Escal barrier film with Ageless RPA oxygen scavenger developed by Mitsubishi Gas Company. These two separate methods were chosen because the presence of little or no obvious pyrite warranted a simple protection; the former method was also more cost effective than the latter.

A note on health and safety

Ammonia gas is both toxic and flammable. Acetone is an irritant to the eyes and skin, particularly following prolonged exposure. Injecting consolidants into specimens with a syringe bears numerous hazards. All work involving the chemicals and processes mentioned in this article was undertaken, following the recommendations of COSHH and risk assessments, with appropriate personal protective equipment and in a ventilated fume cupboard.

Conclusions

The importance of the type collection of Jurassic ammonites meant that the long-term preservation of these fossils was best achieved by combining replication of the fossils with effective pyrite treatment and repackaging. Casting each specimen will eventually lead to more than doubling the size of this collection, as, in addition to the fossils, moulds and casts now also have to be stored. Space in the type collection is very much restricted, and it was decided to keep the casts in a separate store. An additional benefit of replication is to make the collection more usable, for example, in handling sessions, as the originals are too fragile to handle. The use of an antifoaming agent in conjunction with Jesmonite improves the quality of casts. In that sense, Infacol is 'suitable from birth onwards' - up to 155 million years.



Fig. 4. Storage of treated ammonites in micro-environments side by side with untreated specimens.

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