DANGERS TO MALACOLOGICAL COLLECTIONS:
BYNESIAN DECAY AND PYRITE DECAY

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Abstract.—Specimen deterioration in museum collections and exhibits is a recurring worry of curators. Malacological collections, i.e., those containing mollusk shells, are of special concern, because these specimens are composed largely of calcium carbonate, a compound that easily deteriorates in acidic storage media. There are two main problems related to the presence of volatile acids in collections: Bynesian decay and pyrite decay. In Bynesian decay, acetic and formic acids, among others, are released by the materials used to store the collection: wood, varnishes, resins, paper, cardboard, and other storage materials. Under high relative humidity and inappropriate temperature, the acids react with the shells’ carbonate, yielding salts and carbon dioxide. Pyrite decay is similar in appearance: fossil specimens may contain pyrite (FeS₂), which in high relative humidity is oxidized, yielding sulfuric acid and other products. This acid corrodes other shells, including carbonatic fossils. The damage caused is irreversible, but there are methods to avoid or mitigate it. The collection should be kept in conditions of low relative humidity (45–50%) and appropriate temperature range (16–21°C). The use of archival materials, such as steel drawers and cabinets with electrostatic coating, is mandatory. Specimens containing reactive pyrite must be kept in archival-quality plastic containers or closed glass containers. Damaged specimens must be immediately removed and only returned to the collection after proper cleaning.

INTRODUCTION

The deterioration of specimens in enclosed environments, such as the cabinets of natural history collections and exhibits, is a recurring concern of curators and collectors alike. Malacological collections, i.e., those containing molluscan shells, are of major concern, for the specimens are composed largely of calcium carbonate (CaCO₃), a compound that can deteriorate in the presence of acidic vapors (Sturm 2006). However, any other carbonatic specimens may also be damaged by acids: eggshells, carbonatic fossils, carbonatic minerals, rocks, and even archeological and historical art objects (Nicholls 1934, Tennent and Baird 1985, Shelton 1996, Ryhl-Svendsen 2001, Bradley 2005).

There are two main dangers related to the presence of volatile acids in collections: Byne’s disease (also called Bynesian decay) and pyrite disease (also called pyrite decay or pyrite oxidation). Byne’s disease is seen in disfigured shells covered by a thin white granular layer of efflorescing salts and was initially associated with bacterial action, hence the name. However, further studies revealed its real nature as a simple physicochemical reaction related to high relative humidity and inappropriate temperatures in collections: volatile acids corroded the carbonatic shells and fossils, thus causing irreversible damage (Sturm 2006). Curiously, although historically it was never related to bacterial or fungal action, curators commonly refer to the oxidation of pyrite in collections as “pyrite disease.”

These “diseases,” however, are not as extensively known as one would expect given their good documentation (a large portion of this documentation, though, has restricted circulation). This is especially true in developing countries, where many collections unfortunately have less than adequate storage environments. With this thought in mind,
we present here a short historical account of the problems, briefly explaining their physicochemical aspects (even simulating Bynesian decay in the laboratory) and, more importantly, offering many ways to prevent or mitigate their action. In this paper we opted for the terms “Bynesian decay” and “pyrite decay” (following Sturm 2006), for the previous terminology of “diseases” gives the wrong idea that they are caused by biological agents and can be transmitted from one specimen to another.

**Bynesian Decay**

The first mention of Bynesian decay was rather brief, simply reporting the deterioration of shells in collections in the form of a “chalky appearance,” which is now known to be a common feature in affected specimens (Brown 1883). It was followed by another short report that commanded attention to the thin white layer covering the shells (Kenyon 1896 apud Shelton 1996). The subject only gained more notoriety through the work of the amateur conchologist Loftus St. George Byne (1899), who described affected shells and hypothesized that the disease had bacterial origin and could be transmitted from one shell to another. Researchers accepted Byne’s conclusions, although disputing some of his claims, and the idea that the disease had bacterial origins was never questioned, which popularized the term “Byne’s disease” (Shelton 1996). Nicholls (1934) published a work reporting the liberation of acidic gases in wood cases but did not link it to Bynesian decay. Many malacologists still thought of the disease as bacterial until recently, when Tennent and Baird (1985) elucidated its cause and physicochemical mechanisms of action.

**Physicochemical Processes**

Bynesian decay is the result of volatile acids, mainly acetic and formic acids, reacting with the calcium carbonate of shells and other carbonatic materials, such as some fossils. These acids result from the decomposition of wood and other components of the collection’s storage media, such as paper, cardboard, cabinets, cases, drawers, and paints and varnishes (Tennent and Baird 1985, Bradley 2005, Sturm 2006). Acetic acid is formed naturally by the hydrolysis of the acetyl groups of the wood’s hemicellulose, while formaldehyde (the precursor of formic acid) is originated by degradation of lignin or urea-formaldehyde based resins, commonly employed as adhesive in composite wood (Berndt 1987, Bradley 2005). The liberation of acidic vapors by these materials is greater in high relative humidity and high temperature (Bradley 2005).

Because calcium carbonate shows basic properties, it reacts with the volatile acids originating in carbon dioxide, water, and calcium salts (calcium acetate or formate), as represented in a simplified manner by the following equations:

\[
2\text{CH}_3\text{COOH} + \text{CaCO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{Ca(CH}_3\text{COO)}_2
\]

\[
2\text{CH}_2\text{O}_2 + \text{CaCO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{Ca(HCOO)}_2
\]

The intensity of both reactions is directly affected by temperature and relative humidity: the higher the temperature and/or relative humidity, the faster they occur (Sturm 2006).

The result of such reactions is called efflorescence, i.e., salt deposition on a surface (Tennent and Baird 1985). The calcium salts crystallize on the surface of the affected specimen, with the crystals showing a laminar disposition (very thin sheet-like crystal layers stacked one atop the other). This results in the characteristic white encrustation
(Fig. 1E), similar to a fungal or bacterial infestation, that led the first researchers to think of it as a disease (Shelton 2008).

Moreover, the presence of a water layer on the shell’s surface allows the reaction of \( \text{CaCO}_3 \) with the acids to occur even on layers below the surface (Al-Hosney et al. 2005). Without moisture, however, the salt layer formed on the surface acts as a barrier to further deterioration (Al-Hosney et al. 2005). This is a situation in which high relative humidity can lead to increased specimen deterioration.

In order to understand a specimen affected by Bynesian decay, we simulated this condition in the laboratory following a simple procedure. Voucher specimens from this experiment were deposited in the malacological collection of the Museu de Zoologia da Universidade de S\’ao Paulo (MZUSP; S\’ao Paulo, Brazil). A piece of cotton saturated with a 10% acetic acid solution is placed at the bottom of a hermetically closed 100 ml glass container. Although high concentrations of acidic vapors of up to 3000 \( \mu \text{g/m}^3 \) can be found in collection drawers (Kontozova 2002), ours is intentionally much higher (estimated at \( 1.049 \times 10^7 \mu \text{g/m}^3 \)) to accelerate the decaying process, which normally takes months or even years to occur. On top of the cotton, a screen is placed and, above it, the shell. Temperature levels are deliberately uncontrolled in order to simulate a worst-case scenario, where no controlling devices are available. This was done for a bivalve shell (\textit{Amiantis purpuratus}, Veneridae; MZUSP 101934) for 1 month, and salt deposition could already be observed on the second week: Figure 1A–E shows the shell before, during, and at the end of the treatment, with each photo taken precisely 1 week after the previous one. Shells affected by Bynesian decay are grossly disfigured and lose many important characters, posing a considerable problem for taxonomic and systematic studies.

The same procedure was followed for a bivalve shell possessing a thick periostracum (Fig. 1F–J): \textit{Corbicula fluminea} (Corbiculidae; MZUSP 52871). Since the periostracum is an organic layer, composed of proteins known as conchiolin, no salts were formed, and thus there was no efflorescence. However, any shell surface area not covered by the periostracum was affected.

\textit{Dealing with Affected Specimens}

The damage done to the specimens is permanent and irreversible: the calcium carbonate is consumed by the action of the acids, producing one or more salts, carbon dioxide, and water. When an affected specimen is identified in the collection or exhibit, it must be immediately removed from its place and properly cleaned. The cleaning process must be carefully done, for affected shells may be in a very fragile state. Fortunately, this can usually be easily achieved by simply brushing the specimen gently under running water to remove all the salt (Fig. 2). Specimens that are especially fragile may require dry brushing because running water or prolonged soaking may cause further damage (Shelton 2008). After cleaning, the specimen must be moved to a better storage environment; otherwise, Bynesian decay may start again. Of course, the conditions of the entire drawer or case where the specimen was found must also be reassessed and upgraded as needed. The occurrence of Bynesian decay must be recorded in the specimen’s records for future reference. Other ways proposed in the literature for dealing with affected specimens besides cleaning them with water must be disregarded, since they are ineffective or even harmful. These include employing Vaseline, alcohol, antiseptics, caustic compounds, heating, boiling, freezing, and microwaving, among others (Shelton 1996, 2008).
Figure 1. Effects of Bynesian decay simulated in laboratory on a shell of (A–E) *Amiantis purpuratus*, Veneridae, and (F–J) *Corbicula fluminea*, Corbiculidae. (A, F) Intact shells. (B–E) (G–J) Shells after treatment. (B, G) 1 week, (C, H) 2 weeks, (D, I) 3 weeks, (E, J) 4 weeks.
Preventing Bynesian Decay

The most efficient method for avoiding Bynesian decay is making sure that all specimens are stored in an archivally sound environment, with proper storage and temperature/relative humidity conditions, allowing preservation for a virtually indefinite time. Therefore, storage materials that are not of archival quality must be avoided, and environmental conditions such as relative humidity and temperature must be carefully controlled. A comprehensive list of inappropriate materials (and suggestions for possible substitutes) can be found in Table 1.

Storage materials should not liberate acidic vapors. Using cabinets, cases, and drawers made of wood is discouraged, but since this sometimes is unavoidable, woods with low rates of acid liberation are suggested: poplar (*Populus* spp.), hazel (*Corylus* spp.), balsa (*Ochroma pyramidale*), mahogany (*Swietenia* spp.), walnut (*Juglans* spp.), spruce (*Picea* spp.), basswood (*Tilia* spp.), and birch (*Betula* spp.) (Sturm 2006). Still, it is much better

Table 1. List of inappropriate materials (that liberate acidic vapors) for use in collections and exhibits, followed by suggestions for possible substitutes.

<table>
<thead>
<tr>
<th>Potentially dangerous materials</th>
<th>Safe materials</th>
</tr>
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<tbody>
<tr>
<td>Common inks</td>
<td>Carbon-based inks</td>
</tr>
<tr>
<td>Common oil-based varnishes and paints</td>
<td>Water-based varnishes and paints</td>
</tr>
<tr>
<td>Common paper</td>
<td>Archival-quality paper (acid-free, alkalinized/buffered, low lignin)</td>
</tr>
<tr>
<td>Common plastics, polyvinylchloride (PVC), polyurethane, polystyrene</td>
<td>Polyethylene, polypropylene, polycarbonate, polyethylene terephthalate (PET), polytetrafluorethylene (Teflon®)</td>
</tr>
<tr>
<td>Cotton, cork, cardboard, ethylene vinyl acetate (EVA)</td>
<td>Polyester fiberfill, expanded polyethylene foam</td>
</tr>
<tr>
<td>Wood, plywood, particle board, fiberboard, masonite</td>
<td>Steel (with powder coating)</td>
</tr>
</tbody>
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Figure 2. Same specimen of *Amiantis purpuratus* from Fig. 1. Shell after 4 weeks of treatment and washed to remove the salt layer. This represents what is commonly expected of a shell affected by Bynesian decay.
to use steel cases, preferably with an electrostatic powder coating. Many paints, varnishes, and resins (particularly those that are acetate-based) liberate acidic vapors (Tétrault and Stamatopoulou 1997). If an electrostatic powder coating is not possible, then the use of water-based paints and varnishes is suggested instead (Sturm 2006). Other materials commonly found in collections that should also be avoided are: acidic nonarchival cardboard containers and labels, ethylene vinyl acetate (EVA), polyvinylchloride (PVC), formalin, adhesives (based on polyvinyl acetate or formaldehyde), and cotton waste.

Since relative humidity is one of the main factors for the initiation of the chemical reactions of Bynesian decay (Bradley 2005), relative humidity control is of utmost importance. The best way of doing so is using heating, ventilation, and air conditioning (HVAC) inside collection rooms. One should also consider using silica gel or other desiccant materials (such as montmorillonite clay and molecular sieves) inside drawers and containers (Sturm 2006, Shelton 2008). Montmorillonite clay is a natural mineral adsorbent substance that retains water and is used in industry in catalytic processes, water sealing, and as anticaking agents in animal feed. Molecular sieves are man-made porous crystalline silicate materials commonly employed in industry (petroleum and pharmaceutical among others). They act as traps for water molecules, thus retaining environmental humidity (depending on the diameter of their pores, they can retain additional substances).

Relative humidity must be maintained at about 50% or under, but rates of less than 40% can damage delicate specimens (Williams and Hawks 2005, Sturm 2006, Shelton 2008). It must never exceed 70% (Shelton 2008) because excessive moisture favors organisms such as fungi, bacteria, and insects, which are causal agents of biodeterioration (Viitanen 2011).

Temperature is another important factor because all chemical reactions are faster in higher temperatures (Bradley 2005, Sturm 2006). Therefore, it must also be kept under control, and fluctuations should be avoided. For malacological collections, the ideal value is between 16°C and 21°C (60.8°F to 69.8°F), which fortunately is also a good temperature for people to work inside collection rooms (Sturm 2006). Appropriate temperature can be maintained with HVAC systems in continuous operation.

When a completely archival environment cannot be achieved, as unfortunately is the case for many museums, a few mitigating techniques can be employed. Periodically ventilating the collection environment helps to remove any acidic vapors present inside the cabinets and cases, but often this is not an easy task. Some easily available materials can absorb these vapors. Broekerhof (1998) suggests the use of filter papers soaked with a solution of potassium hydroxide (KOH) of approximately 0.14 g of KOH for each 1 g of filter paper. To know when the filter paper must be changed, one must check for its loss of alkalinity with a chemical indicator such as bromothymol blue. Cruz et al. (2008) present other alternatives for absorbing acidic vapors: activated carbon and zeolites, the previous being most commonly available. These materials efficiently absorb vapors but quickly lose efficiency, needing to be changed periodically. A quantity of 3.3 kg of activated carbon per cubic meter is recommended, which lasts for about 2 months and reduces the damaging effects of acidic vapors by 50% to 70%.

**Pyrite Decay**

It is not unusual to find molluscan fossils containing pyrite (FeS₂), especially nautiloids and ammonoids (Fig. 3), from North American and European fossiliferous deposits.
However, keeping such specimens enclosed in collections or exhibits may result in the so-called pyrite disease (also called pyrite oxidation or pyrite decay). Despite its name, it can also happen with fossils and rocks containing marcasite (FeS$_2$), a polymorph of pyrite that is also susceptible to oxidation (Howie 1992, Shinya and Bergwall 2007).

Pyrite decay has been known for almost as long as there have been mineral collections (Bannister 1933, Jerz and Rimstidt 2004), but the problems it poses for fossil specimens (and for other items in collections, biological or otherwise) have received attention only more recently (Oddy 1977, Cornish and Doyle 1984, Birker and Kaylor 1986, Shinya and
Bergwall 2007). As in Bynesian decay, pyrite “disease” is not actually a disease in the sense that it is caused by bacterial or fungal action, but rather it is a common physicochemical process. However, curators around the world have chosen to refer to the oxidation of pyrite in collections as “pyrite disease,” and the name is still in usage. This term should be replaced by one of the more correct terms “pyrite oxidation” (proposed by Shinya and Bergwall 2007) or “pyrite decay” (proposed by Sturm 2006; and also used here). Still, it is relevant to note that pyrite oxidation can also be caused by the iron-oxidizing bacterium *Thiobacillus ferrooxidans*, but this only happens above 95% relative humidity (Silverman 1967, Howie 1992, Jerz and Rimstidt 2004). Because such a high relative humidity should not be a problem for collections and exhibits (and bacterial pyrite oxidation does not produce acids; Silverman 1967), only the common inorganic pyrite decay will be treated here.

*Physicochemical Processes*

Pyrite decay can only happen in the presence of oxygen (it is also called “pyrite oxidation”) and is accelerated by the presence of water in high relative humidity (Borek 1994, Shinya and Bergwall 2007). In these conditions, the decay happens rapidly, as summarized by the following equation (this equation is extremely simplified, since our intent here is simply to explore the overall reaction and its consequences for the collection; for the whole oxidation process, see Rimstidt and Vaughan 2003):

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

The resulting sulfates vary depending on the exact mineral composition of the fossils (and the rock matrices that contain them), time of exposition of the fossil to oxygen, and relative humidity; sulfuric acid, though, is always produced (Borek 1994, Thomas et al. 2003, Shinya and Bergwall 2007). The rate of oxidation diminishes with time, while a thin layer of deposited solids grows on the pyrite’s surface and retards the action of the oxygen (Jerz and Rimstidt 2004). However, in a relative humidity of less than 95%, these same solids can be deposited inside the specimen’s cracks, wedging it apart with time; this enlarged surface area will make the oxidation start anew and further weaken the specimen (Jerz and Rimstidt 2004).

The sulfuric acid produced by the pyrite’s oxidation may be vaporized in ambient temperature and react with the calcium carbonate of shells and carbonatic fossils in a manner resembling Bynesian decay. This reaction produces carbon dioxide, water, and a salt (calcium sulfate), as represented in a simplified manner by the following equation:

\[ \text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{CaSO}_4 \]

The occurrence of pyrite decay can be easily identified by the odor of acid (mainly sulfuric) inside the collection’s cabinets and cases. Detecting an oxidized pyritic specimen is easy because of the rust color and the white, yellow, or brownish powder (oxides or iron sulfates) covering the specimens (Oddy 1977, Shinya and Bergwall 2007). Other specimens that are affected by the sulfuric acid vapor show a white encrustation (generally calcium salts), as in Bynesian decay (Sturm 2006, Shinya and Bergwall 2007).

*Dealing with Affected Specimens*

Pyrite decay actually poses two problems (in both cases, the effects are irreversible): (1) if the pyrite is oxidized, the fossil containing it will be compromised or destroyed; (2) the
sulfuric acid vapor produced by the oxidation may attack other shells and carbonatic fossils in the collection, in a manner similar to Bynesian decay. Affected specimens of the last case may be treated in the same way as Bynesian decay (as described above), so we will deal here only with the former.

Detecting an oxidized specimen is easy because of the usual efflorescence and stains (white, green, yellow, or brown), but cleaning it may pose some difficulties. Sometimes it is possible to clean affected specimens by brushing them under alcohol, but this may not always work. If it does not work, there are two alternative treatments commonly suggested in the literature (using either ammonium vapor or ethanolamine thioglycollate), which do not contain water (otherwise, the oxidation reaction would be favored and the specimen would be further damaged).

The treatment with ammonium vapor neutralizes the sulfuric acid and consists of placing the affected specimen on top of (but not in contact with) a solution of ammonium hydroxide (10% volume) in polyethylene glycol; everything must be enclosed in a glass chamber (Bannister 1933, Rixon 1976, Birker and Kaylor 1986, Howie 1992, Shinya and Bergwall 2007). When the sulfuric acid patches have acquired a rust color, the treatment is completed, and the specimen must then be cleaned with alcohol.

The other treatment, using ethanolamine thioglycollate, may be more efficient than ammonium vapor because it neutralizes sulfuric acid and also removes oxidation products (Cornish and Doyle 1984, Cornish 1987, Shinya and Bergwall 2007). Two methods for this treatment can be found in the literature (Cornish and Doyle 1984, Cornish 1987, Shinya and Bergwall 2007): (1) immersion in a 2–5% ethanolamine thioglycollate solution (in ethanol or isopropanol), for up to 4 hours (repeating it after cleaning the specimen, if necessary); (2) covering the affected regions of the specimen for up to 3 hours with a paste prepared with a 3–5% ethanolamine thioglycollate solution (in ethanol or isopropanol) mixed 1 : 1 with magnesium silicate (sepiolite). In both cases, the specimen must be afterward cleaned with alcohol.

In all the cases described above, the treatments are only meant for cleaning the specimens. They will not prevent further pyrite decay. Therefore, the affected specimens should be returned to a collection with more appropriate relative humidity and temperature conditions.

Finally, the sulfuric acid produced in pyrite oxidation can also damage other materials found in collections, such as specimen labels and cardboard or plastic containers, sometimes completely ruining them. While containers can be replaced, labels contain valuable information that can be lost forever (this is especially true for labels of older specimens, whose data may not be archived in computer databases). Stooshnov and Buttler (2001) provide a simple way for dealing with affected labels, recovering part of their data and protecting them from further harm: labels must be manually cleaned with water and brushing, then deacidified by two mutually exclusive methods: either a magnesium bicarbonate solution (50%, in water) for 30 minutes or a deacidification solution (methoxy magnesium methyl carbonate solutions available for sale as liquids or sprays).

Prevnting Pyrite Decay

As stated above, pyrite decay depends upon the presence of oxygen and a high relative humidity; therefore, the first step to minimize its occurrence is controlling relative humidity in collections storage. As noted by Shinya and Bergwall (2007), controlling relative humidity is far more important than controlling oxygen. A relative humidity
lower than 50% is recommended, but it must be remembered that values below 40% can damage some specimens (Williams and Hawks 2005, Sturm 2006, Shinya and Bergwall 2007, Shelton 2008). Relative humidity can be controlled by the same methods described above for Bynesian decay.

Contact of oxygen with specimens containing pyrite can result in oxidation (sometimes even within the recommended relative humidity range), but dealing with oxygen is actually less problematic than it might seem at first glance. In theory, exposure to oxygen must only be avoided for those specimens containing reactive pyrite. There are nonreactive morphs of pyrite, but since their identification is not always obvious (and they should be constantly monitored anyway), the most practical way is to treat every fossil containing pyrite in the same way: they should be isolated in microenvironments. The most obvious and practical way to achieve this is by enclosing them (preferably together with silica gel or other desiccant to also keep humidity in check) in a small container, where the oxygen is not renewed. Although glass and archivally sound plastic containers are the most practical option, other containers that are impervious to moisture and oxygen may also be used, including barrier films and air-tight packs (Shinya and Bergwall 2007). Despite being more expensive, these options offer better protection for the specimens, especially the air-tight packs. To further avoid contact between specimen and oxygen, some forms of coating have been proposed by previous authors, but these treatments are ineffective and sometimes may even damage the specimens, so they are not recommended (Howie 1992, Buttler 1994, Sturm 2006, Shinya and Bergwall 2007).

**Concluding Remarks**

It is hard to come up with a universal solution for all the problems a conchological collection might face, especially to reconcile the different ideal requirements of relative humidity and temperature in order to avoid both Bynesian and pyrite decay. Since the damage caused by these phenomena is irreversible, the best solution is to avoid them in the first place. First and foremost, the collection must be kept in conditions of low relative humidity (preferably between 45% and 50%; never lower than 40% and never exceeding 55%) and appropriate temperatures (between 16°C and 21°C); this can be easily achieved with HVAC systems and the use of common desiccant materials such as silica gel. Ventilating the collection from time to time is also a good preventive measure. The combined use of hygrometer, thermometer, and pH indicators is recommended to monitor, respectively, relative humidity, temperature, and acidity levels, so it can be easily seen when the conditions in the collection are not appropriate. Other precautions include the use of materials that do not liberate volatile acids with time, such as steel cabinets painted with electrostatic powder coating. Finally, specimens that contain pyrite must be kept preferentially in closed containers.

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**Literature Cited**


