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Bynesian efflorescence in the Țării Crișurilor Museum's zoological collection

Erika POSMOŞANU and Dorina GOLBAN

Muzeul Ţării Crişurilor, Oradea, Calea Armatei Române nr. 1A, 410087
e-mail: eposmosanu@gmail.com

Abstract. The Bynesian efflorescence occurs especially on carbonate-based specimens in natural history collections as result of acidic vapors dissolved in the atmospheric water which react with specimens. Although this phenomenon is well-known worldwide, it is almost unknown in Romania. Țării Crișurilor Museum has lost its ownership over its former headquarter in 2006 and has undergone a complex relocation process. All the museum's collections were prepared for transportation, being kept in sealed packed storage for over a decade. The Bynesian efflorescence was observed on three clutches from the oology collection and on one unmounted skeleton of *Lepus europaeus*. All the affected specimens showed organic matter left on their surfaces, due to improper preparation. The best result of cleaning the specimens was obtained by first brushing off the salt crystals and washed under running distilled water afterwards. The malacological collection is not affected by Bynesian efflorescence.

Keywords: Oology, mammal skeleton, Bynesian efflorescence, Conservation

Abbreviation: MTCO – Tării Crișurilor Museum Oradea.

Introduction

The Natural History Department's collection consists of 158.676 registered specimens, of which over 49.000 items are in the zoological collection. The latter includes a great variety of dry and wet specimens in the field of entomology, malacology, oology, ornithology, mammalogy and herpetology.

The oology collection contains over 3.600 clutches, coming from Europe, Africa, Asia, North and South America and Australia, with 14.000 specimens, representing 365 genera, 660 species and 579 subspecies. The collection has three main parts. Chronologically the first one comes from Dr. Ernest Andrássy (1894-1968) and contains eggs found in the surroundings of Valea lui Mihai and Erului Valley, as well as clutches obtained by exchange from Brazil, North America, India, Indonesia, Australia and Europe, including Mediterranean and Scandinavian species (Béczy, 1971). The second part of the collection, numerically the most important one, comes from Ladislau Dobay (1873-1943), initially consisting of 2192 clutches with 8770 eggs, representing birds of prey and singing species from Transylvania, collected at the beginning of the 20th century (Béczy, 1971). The rest of the collection is the result of the museum's staff work (Tamás Béczy, Kováts Ludovic and Poliş Rozalia). The most common specimens in the collection are the nesting birds from Romania, as the collection contains 80% of our country's nesting bird species.

The Țării Crișurilor Museum has lost its ownership over its former headquarter (the Baroque Palace) in 2006 and has undergone a complex relocation process. All the museum's collections were packed and prepared for transportation.

Material and method

The oology collection has been stored in specially made wooden cabinets for many years. This collection is the most fragile one, so each clutch, originally placed in a cardboard box, was packed in bubble wrap, and placed in the original storage cabinets, to prepare it for relocation. Due to some political issues, the relocation succeeded only in 2019. The oology collection was transported to the new location in the original storage cabinets and was finally unpacked in 2022, after eighteen years of sealed storage.

Generally, the collection was in good conservational state, but 3 clutches, out of 3600, presented a moldy appearance. All three clutches have been stored in the same type of cardboard boxes, two of them representing eggs of *Perdix perdix* (MTCO 9443/$_{1-4}$ – Fig. 1. and MTCO 9446/$_{1-5}$ – Fig. 2). The third clutch with ten eggs is unlabeled, has no register number, nor any data regarding its collection, preparation, or taxonomy (Fig. 3). Microscopic analyses of these eggs showed that the mold-like white powder had a salty, crystallized appearance.

After thorough documentation, we concluded that the eggs showed Bynesian efflorescence. The Bynesian efflorescence is quite common in natural history collections, especially affecting carbonate-based specimens, but very little is known about it in Romania. Although there are lots of papers dealing with it in the international literature (Byne, 1889; Anew, 1981; Tennent and Baird, 1985; Carter, 2000; Rhyl-Svenden, 2001; Callomon, 2002; Shelton, 2008; Callomon and Rosenberg, 2012; Cavallari et al, 2014; Curran and Pouliot, 2015; O'Neil, 2015; Hairie et al, 2020), we couldn't find any paper regarding its occurrence in Romanian Natural History Collections.

The Natural History Department's conservator (D.G) has checked the carbonate-based specimens from the zoological collection for Bynesian efflorescence, especially the malacological collection. Fortunately, none of the specimens showed any sign of this type of efflorescence.

The Bynesian efflorescence was observed on the surface of a single specimen from the mammalogy skeletons collection, consisting of *Lepus europaeus* skeletal elements (MTCO 10.224 – Fig. 4). The skeletal parts were kept in a cardboard box, deposited in a wooden cabinet since its preparation in 1956.

Brief history of the Bynesian efflorescence

The corrosion of mollusk specimens was first mentioned by Brown (1883) in the mid-18th century but the first description of the salt efflorescence, known as Byne's "disease", was given by Sir Loftus St. George Byne (1872-1947), an amateur conchologist. Byne analyzed the shells from the malacological collection of South Kensington National Collection and observed the following: the shells in the drawers are either partially or entirely destroyed, their surface being corroded and covered by a fine white powder, card mounted specimens were more affected, it didn't extend to every specimen in a drawer, affected shells were 20-50 years old and the destruction has travelled from shell to shell, from drawer to drawer, like a disease (Byne, 1899). He assumed that the white powder on shell surface was calcium butyrate, sometimes mixed with calcium acetate and he thought that butyric acid is the product of the fermentation of animal matter, remains of the soft parts inside of the shell, due to incorrect preparation. He incorrectly thought that the deterioration of shells was caused by bacterial attack and that it could be transmitted from one shell to another like a disease (Shelton, 2008).

The corrosion of carbonate-based specimens was many years improperly referred in the literature to Byne's "disease" (Tennent and Baird, 1985; Callomon, 2002, Shelton, 2008; Callomon and Rosenberg, 2012). The more correct terminology to describe this condition is Bynesian decay or Bynesian efflorescence (Ryhl-Svendsen 2001; Cavallari et al, 2014; Curran and Pouliot, 2015).

The cause of the Bynesian efflorescence is the acidic vapors dissolved in the atmospheric water which react with specimens made of calcium carbonate: Mollusca shells (Tennent and Baird, 1985; Carter, 2000; Callomon, 2002; Shelton, 2008; Callomon and Rosenberg, 2012; Cavallari et al, 2014; O'Neill, 2015), cuttlebones (Curran and Pouliot, 2015), foraminifera shells (Hairie et al, 2020), eggshells (Anew, 1981; Ryhl-Svendsen, 2001, O'Neill, 2015) and bones (O'Neill, 2015). As a result of this reaction calcium acetate and calcium formate, or a mixture of those two, are crystalized on the surface of the specimen irreversibly damaging it (Anew, 1981; Tennent and Baird, 1985; Shelton, 2008; Callomon and Rosenberg, 2012; Cavallari et al, 2014; Curran and Pouliot, 2015). All these recent studies concluded that the chemical reaction is favored by an acidic environment plus high relative humidity (RH) and inappropriate temperature (Smedemark and Ryhl-Svendsen, 2022). Affected specimens initially show white patches on their surface, but with the progress of the decay the patches or spots turn into a moldy-looking appearance.

The first analyses of the white efflorescence on eggshells were provided by Anew (1981). Anew used electron microscopy, which showed a mass of intergrown crystals, and IR spectrophotometry to identify an impure hydrated calcium acetate, confirmed by NMR analyses, but also showed the presence of organic matter, associated with the cuticles of the shell (Anew, 1981). He also noted that the most affected eggs have been donated in an advanced stage of incubation at the time of collecting, lacking any information on the process of blowing the eggs and removing embryonic material. Anew (1981) also performed the first experimental study, using chicken eggshells exposed to acid vapors in 80% RH environment, concluding that there is a relationship between surface texture of the eggs, the rough to chalky appearance, and the occurrence of salt efflorescence, the glossy surfaces being less affected. He also noted that the attack occurred mostly in the areas with defects in the structure of the eggshell (Anew, 1981).

Norman Tennent and Thomas Baird (1985) analyzed the efflorescence by means of several techniques: x-ray diffraction (XRD), infrared (IR) spectroscopy, thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR) spectroscopy, identifying calcium acetate, calcium formate, as well as a mixed acetate-formate salt. They also indicate the cause of deterioration by acetic and formic acid vapors, liberated by wooden, primarily oak, storage cabinets (Tennent and Baird,1985).

During our documentation process we found useful information on the "Indoor Air Quality in museums and archives" web site (iaq.dk) which contains valuable data for those interested in the deterioration processes in cultural heritage objects caused by the indoor environment, especially air pollutants. Ryhl-Svendsen (2001) has a case study on this website regarding Bynesian efflorescence on an eggshell, in which he presents an experiment on two hen eggshells, exposing one eggshell to acetic acid and high humidity environment. The exposed shell showed calcium acetate efflorescence on its entire surface after a month and eventually the shells crumbled to dust in the acidic environment (Ryhl-Svendsen, 2001).

Cavallari et al. (2014) also simulated acidic conditions in the laboratory exposing two different bivalve shells for one month and observed that the specimens affected by Bynesian decay have lost many of the important features, which are commonly used in taxonomic or systematic studies. To avoid the accumulation of acidic vapors the above authors recommended periodical ventilation of the collection, progressive removal of cardboards, cork and other non-treated cellulose derivate and replace with more appropriate materials; permanent control of RH and T values; the use of activated carbon, zeolithes or filter paper soaked in a solution of potassium hydroxide (Cavallari et al, 2014).

Microscopic observations

Altough all the eggshells were kept in the same type of cardboard, they were affected by corossion differently, the efflorescence consisting of white salt crystals being distributed unevenly on the surface of the egghells. Unfortunately, we couldn’t find any record of the preparation process, nor information on blowing the eggs or the way they were cleaned.

We analysed all the affected eggshells as well as the surfaces of the bones of the *Lepus europaeus* specimen. Microscopic analyses were performed using Nikon SMZ 800 binocular microscope.

The salt crystals formed a quite thick layer on the specimen’s surface, distributed unevenly on the analyzed area (Fig. 5). We did not perform chemical analyses to determine whether the salt efflorescence is calcium acetate or calcium formate, or a mixture of these two, but we preserved some samples for further investigations.

Microscopic analyses of the most affected eggshells showed that all of them had some organic material left on their surface after preparation (Fig. 6). The most probable explanation for the presence of these materials of organic matter is that the preparation of the eggs was not properly finalized. In the case of the unlabeled clutch, there are two crumbled eggshells, with organic material left inside the shells (Fig. 7).

In the case of the skeletal parts of *Lepus europaeus*, the most affected elements are the joint surfaces of the bones, the porous elements of the skull and the teeth (Fig. 8). The smallest parts of the skeleton were kept in two different jars, one perfectly closed and another one with a cotton wool closure. In the case of the second jar, the skeletal elements are all affected by the white, salty efflorescence, which leads us to the conclusion that the cotton wool closure offered a more acidic environment.

Microscopic observation revealed that the affected skeletal parts were not cleaned properly after preparation with hydrogen peroxide. Also, some parts of the surface of the bones, especially in the joint areas, are still greasy, preserving a fine layer of organic matter. The acidic vapors formed by the decomposition of cellulose from the old cardboard box in humid conditions and the organic matter left after improper preparation of the specimen favored the occurrence of the Bynesian efflorescence.

Although the Bynesian efflorescence frequently occurs in mollusk collections worldwide, our malacological collection is not affected, which is excellent news.

Treatment and conservation

The first step after discovering the three affected clutches was to isolate the eggshells in the Lab and maintain a proper microclimate, with Relative

Humidity between 45-55% and temperature 18-21°C. We monitored these values in the Lab on daily spot-checks with a hand electronic thermohydrometer.

Byne (1889) recommended that the affected shells should be soaked for 24 h in a solution of corrosive sublimate (1 part to 1000 water) and then dried. Anew (1981) proposed to clean the affected eggshells by washing in distilled water and drying. The same treatment was suggested by others (Shelton, 2008; Callomon and Rosenberg, 2012; Cavallari et. al, 2014), respectively to wash the specimens in running water or soak them in water, then move the specimens in a dry environment. Carter (2000) suggested that corroded specimens should be cleaned by gently brushing off the salt efflorescence.

There is no other treatment than water, the use of alcohol, antiseptics, boiling, freezing, or microwaving in attempt to remove Bynesian efflorescence is not recommended (Shelton, 2008; O'Neill, 2015).

After documentation we applied two different treatments, one clutch (MTCO 9446) was cleaned by running distilled water, the other two clutches (MTCO 9443 and the unlabeled one) were first cleaned by brushing off the salt under binocular microscope and then washed by running distilled water.

The damage made by Bynesian efflorescence is permanent and can be stopped only by cleaning the specimens and keeping them in proper storage conditions. The specimens cleaned directly by running distilled water showed the effect of the corrosion as discoloration of the shell surface and a fine, hard, unevenly crystallized surface. A better cleaning result was attained in the case of the specimens cleaned first by brushing off the white crystals of the salty efflorescence and cleaning by running distilled water afterwards (Fig.9).

The same procedure was applied to the *Lepus europaeus* skeletal parts. Brushing off all the bones under binocular microscope was a time-consuming process, but this procedure was efficient (Fig.10)

After cleaning and drying, the specimens were moved in plastic boxes, the labels were placed in polyethylene sealed-bags, to isolate the old, acidic label and ink.

All the specimens were kept under observation in the Lab for two months, in a controlled environment. After the specimens were stabilized, they were moved to the new storage facility, consisting of coated metal cabinets with metal drawers, following the recommendations given by Shelton (2008) and Cavallari et al (2014). We monitor the storage environment on a daily basis by using a digital hand thermohydrometer, to keep the RH values within 45-55% and temperature between 18-21°C in accordance with Cato (1994).

Conclusions

Bynesian decay sporadically occurred in the Țării Crișurilor Museum's zoological collection. Three clutches in the oology collection and one unmounted skeleton in the mammalogy collection presented Bynesian efflorescence. All the affected specimens showed the presence of organic material due to improper preparation.

The specimens were isolated, cleaned by brushing and by running distilled water, and dried.

The treated specimens were moved into the new, non-acidic storage system, consisting of metal cases and drawers. To avoid acidic vapor formation, we isolated the treated specimens from the acidic environment by using micro-environmental enclosure, such as polyethylene boxes, we also placed the labels in polyethylene sealed-bags. The conservator monitors the microenvironment of the storage room on a daily basis, maintaining RH between 45-55% and temperature between 18-21°C.

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Fig. 1. *Perdix perdix* clutch with 4 eggs, MTCO 9443

Fig. 2. *Perdix perdix* clutch with 5 eggs, MTCO 9446

Fig. 3. Unlabeled clutch with 10 eggs, the most affected clutch, with 2 crumbled specimens

Fig. 4. *Lepus europaeus* unmounted skeleton, MTCO 10224

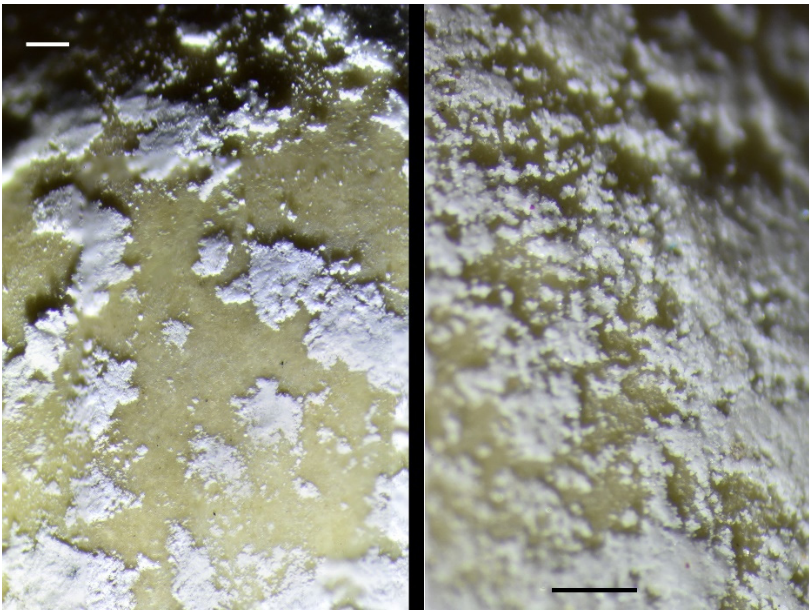

Fig. 5. Details of the eggshell’s surface corroded by Bynesian efflorescence. Line indicates 1 mm.

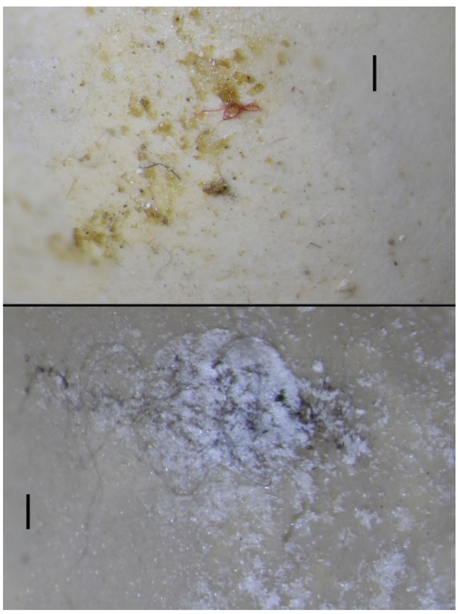

Fig. 6. Organic material left on the eggshell’s surface (A – MTCO 9443/3; B – MTCO 9446/2). Line indicates 5 mm.

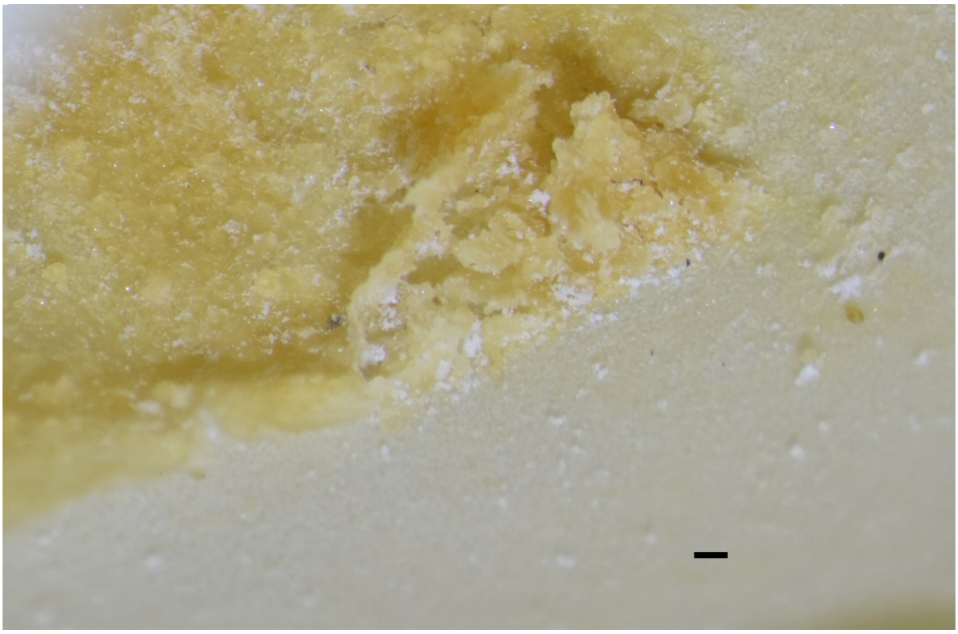

Fig. 7. Thick layer of organic mater inside the most crumbled eggshell. Line indicates 1 mm.

Fig. 8. Bynesian efflorescence on the teeth of *Lepus europaeus* (MTCO 10224)

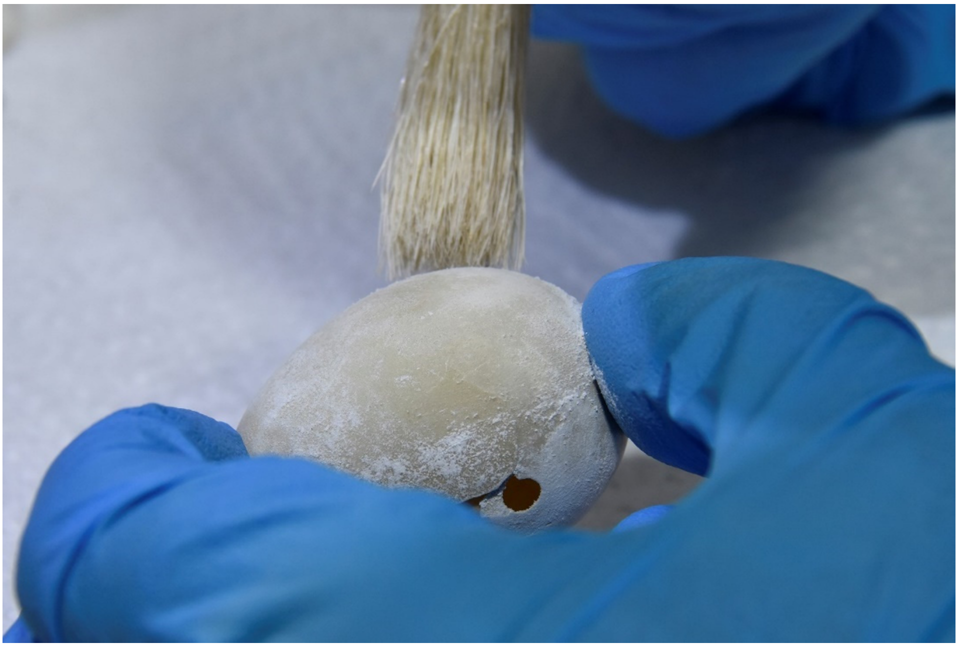

Fig. 9. Brushing off the salt efflorescence.

Fig. 10. Teeth of *Lepus europaeus* after treatment (MTCO 10224)

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