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Byne's decay on microscopic calcareous shells: case study of Alcide d'Orbigny's foraminifera collections stored in Paris and La Rochelle, France

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ABSTRACT
The foraminifera collection of micropalaeontology pioneer Alcide Dessalines d'Orbigny (1802-1857), housed at the National Museum of Natural History (MNHN), Paris, was recently diagnosed with Byne's decay. The condition report presented here establishes that at least half of the foraminifera is affected, with numerous types seriously damaged. A comparison with specimens from the Museum of La Rochelle, also collected by d'Orbigny, and the study of the MNHN archives indicate that the decay is related to the type of mounting and to the poor environmental conditions of the storage.

The emergence of the salts appears linked with a pollution of Volatile Organic Compounds (VOCs) emitted by the wood-derivative materials introduced during the XIXth century (paper and cork) and unappropriated temperature and humidity fluctuations. The study of the damage highlights a correlation between foraminifera sampling site and their current condition, recent to sub-recent specimens collected in marine environment showing more intense degradations than fossil ones. The nature of foraminifera test seems to have also an influence on the degradation, porcelaneous foraminifera being more sensitive to salt crystallizations than hyaline ones. Non-invasive Raman spectrometry enabled to identify degradation products. Calcium acetate or mix acetate-formate salts, that are the most common Byne degradation products, were not detected. Instead, the two polymorphs of calcium formate [the orthorhombic α-$Ca(HCOO)_2$ and the metastable tetragonal β-$Ca(HCOO)_2$] are predominantly present, occasionally with magnesium formate dihydrate [$Mg(HCOO)_2{\cdot}2H_2O$] and calcium lactate pentahydrate [$Ca(CH_3CH\text{-}OH\text{-}COO)_2{\cdot}5H_2O$]. The glass tubes that were exposed to the VOCs are also damaged by crystallizations of sodium formate anhydrate [NaHCOO(II)]. Deeper investigations must be undertaken to better understand the occurrence of these unusual degradation phases and the non-detection of acetates.

KEY WORDS
Byne's decay,
micropalaeontology,
calcium formate,
degradation,
VOC,
collection conservation,
Raman spectrometry.

RÉSUMÉ
Dégradation de Byne sur des coquilles calcaires microscopiques : étude des collections de foraminifères d'Alcide d'Orbigny conservées à Paris et La Rochelle, France
La collection de foraminifères du pionnier de la micropaléontologie Alcide Dessalines d'Orbigny (1802-1857), conservée au Muséum national d'Histoire naturelle (MNHN), est aujourd'hui affectée par la dégradation de Byne. La moitié des foraminifères apparait touchée par la formation de cristaux et de nombreux types sont sérieusement endommagés. La comparaison avec d'autres spécimens recueillis par d'Orbigny conservés au Muséum de La Rochelle, combinée à une étude des archives du MNHN, confirme que cette dégradation est liée au type de montage et aux mauvaises conditions environnementales. Elle provient de l'émission de composés organiques volatils (COV) par les matériaux dérivés du bois (papier, liège) introduits dans les montages du XIX^{ème} siècle et des conditions de température et d'humidité fluctuantes et inappropriées. L'étude des spécimens endommagés montre une corrélation entre le lieu de prélèvement des foraminifères et l'intensité de la dégradation, soulignant que les spécimens récents collectés en milieu marin sont plus affectés que les fossiles. La nature des tests pourrait également avoir une influence sur le type de dégâts, les foraminifères *porcelanés* étant plus sensibles aux efflorescences cristallines que les formes hyalines. Les produits de dégradation ont été analysés par micro-spectrométrie Raman. Les sels d'acétates ou d'acétate-formiates de calcium, considérés comme caractéristiques de la dégradation de Byne, n'ont pas été détectés. Deux polymorphes du formiate de calcium prédominent : la forme orthorhombique α-$Ca(HCOO)_2$ et la forme tétragonale β-$Ca(HCOO)_2$. D'autres espèces mineures ont été détectées : formiate de magnésium dihydrate [$Mg(HCOO)_2{\cdot}2H_2O$] et lactate de calcium pentahydrate [$Ca(CH_3CH\text{-}OH\text{-}COO)_2{\cdot}5H_2O$]. Les tubes en verre, exposés aux COV, ont également développé des cristaux de formiate de sodium anhydre [NaHCOO(II)]. Des études complémentaires doivent être menées pour mieux comprendre la présence de ces sels peu ordinaires et la non-détection des acétates.

MOTS CLÉS
Maladie de Byne,
micropaléontologie,
formiate de calcium,
dégradation,
COV,
conservation des
collections,
spectrométrie Raman.

INTRODUCTION

A pioneer in the field of biostratigraphy, between La Rochelle and Paris

Alcide Dessalines d'Orbigny was behind the first classification of single-celled microorganisms, called "Foraminifera" (Vénec-Peyré & Bartolini 2010). From a young age, he was trained to their observation by his father Charles-Marie d'Orbigny, also a micropalaeontology enthusiast (Legré-Zaidline 2003). Based on his own material, he was able to identify more than 500 species in the *Tableau méthodique de la classe des Céphalopodes* (d'Orbigny 1826). In 1853, he was appointed to the newly created chair of palaeontology at the Muséum national d'Histoire naturelle, Paris (MNHN). His foraminifera collection, which he amassed at least two decades before this nomination followed him from La Rochelle to Paris (Vénec-Peyré 2002). After d'Orbigny's death, in 1858, it was acquired by the MNHN and has since been housed at the Jardin des Plantes in Paris Vth arrondissement. It accounts for about 4000 specimens, both fossil and recent, and includes numerous types (Vénec-Peyré & Bartolini 2010). It also comprises 851 bottles filled with the sands from which the specimens were sampled.

Before moving to Paris, d'Orbigny left some foraminifera specimens to his father who joined this material to the collections of the *Société des Sciences naturelles de Charente-Inférieure,* a learned society created in 1836 in which he was involved. After Charles-Marie d'Orbigny's death, these

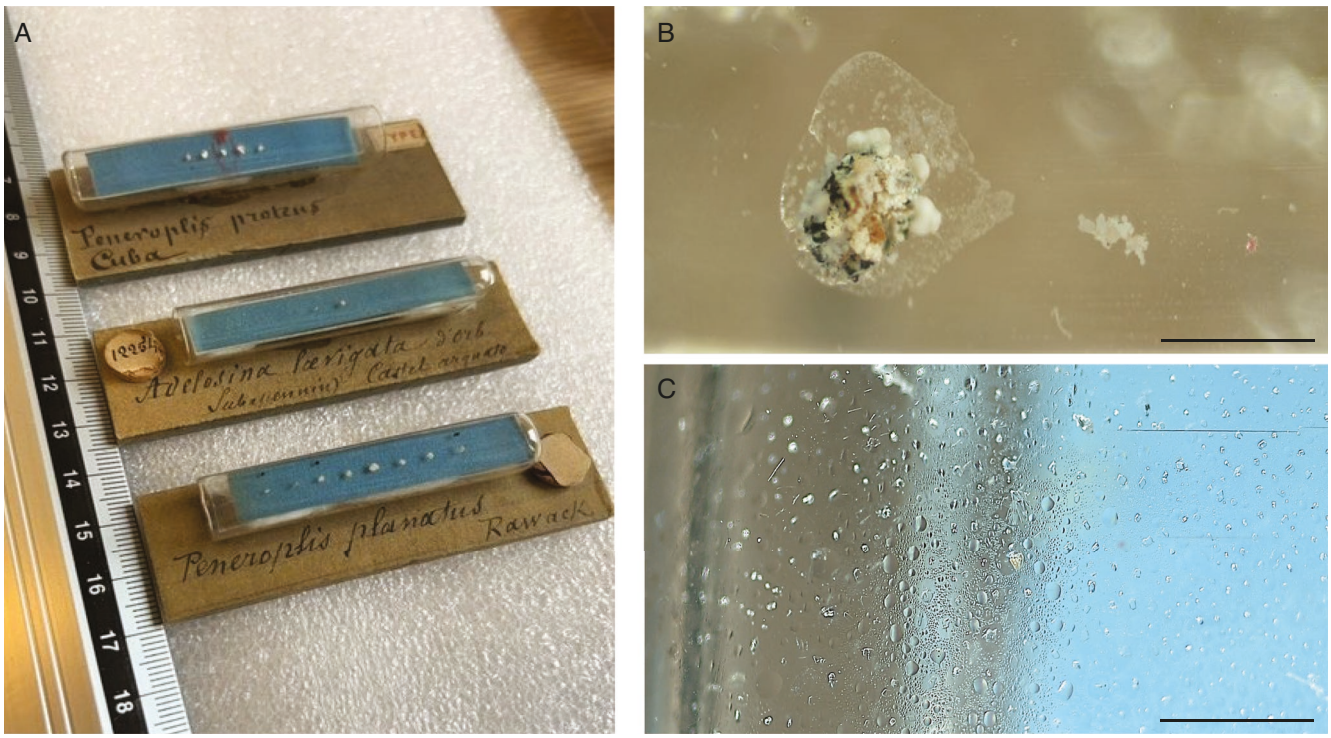


Fig. 1. — Current mountings used for d'Orbigny's foraminifera collections in Paris and examples of alterations. The foraminifera aquired by the MNHN were re-mounted during the 1880s by the micropalaeontologist Olry Terquem. He stuck the specimens on a glass slide that was slid, with blue paper and cotton behind, in a glass tube sealed with a cork (**A**). The emission of VOCs by the storage materials led to the development of Byne's decay on the calcareous foraminifera (here MNHN.F.FO312.2-12, *Cymbaloporetta squammosa* (d'Orbigny, 1839)) (**B**) and also to the formation of 'alteration droplets' inside the glass tubes (**C**). Scale bars: B, 700 µm; C, 1 mm. Photos: A, C. Hairie; B, C, M.-B. Forel.

collections were bequeathed to the Fleuriau museum that later became the Museum of Natural History of La Rochelle. Although smaller, the d'Orbigny's foraminifera collection of La Rochelle skilfully completes the collection housed at the MNHN, Paris.

Up to now, more than 50 000 fossil and living species of foraminifera have been recorded (Hayward *et al.* 2023). They are predominantly marine organisms, with most species being benthic (i.e. living at the surface of or within sea-bottom sediments) and a smaller proportion planktonic (living in the water column). Their unicellular nature was discovered by Felix Dujardin in 1835, a decade after d'Orbigny's classification was published. Foraminifera are today classified as a phylum rank and are generally characterized by micrometric shells of various forms and compositions, which are called "tests". Most of them are made of calcium carbonate (calcite or aragonite), and a few taxa include opaline silica, organic matter, or agglutinated sediment particles. Calcitic tests, made of calcite, can be either of hyaline or porcelaneous nature: they have been explained by two different modes of biocalcification (Hemleben *et al.* 1986; de Nooijer *et al.* 2009). Visually, hyaline tests (e.g. Rotaliida, Nodosariida and Spirillinida) appear translucent thanks to an orderly arrangement and/or a large size of calcite crystals. In contrast, porcelaneous tests (e.g. Milliolida) contain less well-ordered crystals of calcite and higher amounts of magnesium that make them opaque and porcelain-like (Dubicka *et al.* 2018; Dubicka 2019; de Nooijer *et al.* 2023).

Since the pioneering work of d'Orbigny in the development of stratigraphy and palaeoenvironmental studies, fossil foraminifera turned out to be highly useful as biostratigraphic markers in the dating of sedimentary rocks (Lirer *et al.* 2019) or bio-indicators for the study of climatic changes (Waelbroeck *et al.* 2005; Cléroux *et al.* 2008). Because their calcareous tests are very sensitive to environmental parameters (e.g. temperature, pH, salinity, oxygenation), their abundance and diversity in the sediments, their variations in form and size, as well as their isotopic and trace element compositions, are key proxies for the reconstitution of palaeoclimates and palaeoenvironments. Recently, the scientific value of sediment samples collected up to 150 years ago was proved in the assessment of global changes in the seafloor environment (Rillo & Miller 2019; Fox *et al.* 2020). The d'Orbigny foraminifera collection, that gathers sands and specimens from all around the world, thus constitutes an outstanding historical archive for palaeontologists and climatologists.

About Byne's decay

In 2016, a systematic digitization campaign (E-Récolnat project) revealed that many of the mounted specimens were damaged by the growth of crystalline efflorescence. Some of the specimens had become unrecognisable, covered with white efflorescence while others had turned into dust (Fig. 1B).

This type of damage, known as "Byne's decay", is named after the English chemist Lotfus St George Byne who observed it on shell specimens at the end of the XIXth century (Byne

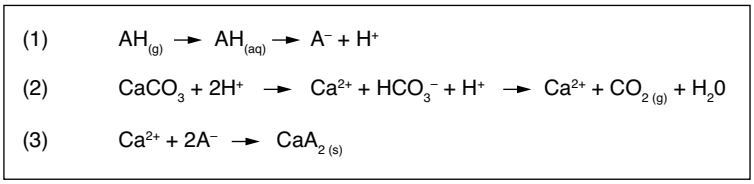


Fig. 2. — Chemical reactions underlying Byne's decay in presence of acetic acid (A = CH3COO) or formic acid (A = HCOO): **1**, dissolution and dissociation of carboxylic acid AH; **2**, dissolution of calcium carbonate in acidic medium; **3**, precipitation of the calcium carboxylate salt CaA_2.

1899). Later, in the 1930s, these alterations were attributed to the presence of acidic species emitted by wooden furniture (Nicholls 1934). Indeed, wood and its derivatives (i.e. paper, cork or cotton) emit pollutants, also called "Volatile Organic Compounds" (VOCs) during their natural aging. Among these, small acids such as formic and acetic acids are considered today as primary indoor pollutants (Nicholls 1934; Arni *et al.* 1965a, 1965b; Tennent & Baird 1985; Gibson & Watt 2010; Paterakis 2016; Adamová *et al.* 2020; Smedemark *et al.* 2020). These VOCs are also emitted by other types of organic materials such as coatings (Stockwell *et al.* 2021), adhesives (Girman *et al.* 1986), plastics and rubbers (Curran & Strlič 2015).

Byne's decay specifically concerns porous calcareous materials submitted to humid and polluted conditions. It is often observed on macroscopic shell collections and sometimes misinterpreted as fungus growths (Cavallari *et al.* 2014). Yet we could not find any report of this type of deterioration dealing with microscopic specimens. The chemistry of Byne's decay, summarized in Fig. 2, relies on the dissolution of volatile acidic compounds (AH) in the condensed water of the porous network. This leads locally to acidic conditions and dissolution of the calcium carbonate matrix. Released calcium ions recombine with available carboxylate species (A^-), provoking the precipitation of calcium-organic salts (CaA_2) (Gibson & Watt 2010).

The mineralogy and physico-chemistry of these salts are still investigated. Formic acid being released by storage materials, the occurrence of calcium formate as degradation by-product could be expected (Grzywacz & Tennent 1994). Yet, to our knowledge, the literature does not mention the formation of pure calcium formate on these calcareous collections, but instead mixed calcium acetate/formate salts and pure calcium acetate species (Paterakis & Steiger 2015; Bette *et al.* 2018, 2019; Eggert *et al.* 2021). Indeed, crystalline growth of calcium acetate mono- and hemi-hydrate [$Ca(CH_3COO)_2{\times}H_2O$ and $Ca(CH_3COO)_2{\times}1/2H_2O$] and mixed calcium acetate-formate hydrate [$Ca(CH_3COO)(HCOO){\cdot}H_2O$] have been identified on shell, fossil and egg collections from different museums (Tennent & Baird 1985; Bette *et al.* 2018, Eggert & Fischer 2021). More complex salts like calclacite [$Ca(CH_3COO)Cl{\cdot}5H_2O$] or thecotrichite [$Ca_3(CH_3COO)_3Cl(NO_3)_2{\cdot}7H_2O$] have also been sporadically observed on ceramics and potteries (Paterakis 1995; Linnow *et al.* 2007; Paterakis & Steiger 2015, Eggert *et al.* 2016). More recently, an unnamed compound of composition $Ca_2(CH_3COO)(HCOO)(NO_3)_2{\cdot}4H_2O$ was identified on ancient attic amphorae and wine jugs (Bette *et al.* 2018).

Two collections, two histories

The collection housed at the MNHN

The history of the d'Orbigny foraminifera collection at the MNHN was recently discussed in an article (Hairie *et al.* 2022). This helped to identify, through the archives of the palaeontology laboratory, the numerous places where the foraminifera were stored during the last 150 years. Yet Byne's decay does not only depend on the climate of the rooms but also on the storage materials. We owe the current mountings to the micropalaeontologist Olry Terquem, who frequented the palaeontology laboratory from 1873 to 1887 and sorted out d'Orbigny's foraminifera (Vénec-Peyré & Bartolini 2010). Specimens of the same species and locality were fixed on a single glass slide, hereafter referred to as a "preparation". Up to fourteen specimens could be found on the same slide. Each of these preparations was placed on a blue paper strip and then sealed in a small soda-lime glass tube with a cork cap (Fig. 1A). With such configuration, the foraminifera remained enclosed in a small volume for decades, in the presence of cellulose-based materials likely to emit VOCs. Damage to specimens was noticed in the middle of the XXth century, and continued to be observed later in the 1990s, leading curators to remove some cork caps to limit condensation due to temperature variations. Yet, nothing was done to investigate the deterioration further, due to a lack of human and financial resources (Hairie *et al.* 2022).

The collection housed at the Natural History Museum of La Rochelle

D'Orbigny's foraminifera housed at La Rochelle are considered in this work because they are contemporary to those of the MNHN. Although fewer in number, they have been preserved in a different environment and therefore have a different conservation history. Most of these foraminifera were mounted by the micropalaeontologist enthusiast Charles Basset at the end of the XIXth century (Basset 1885). Basset was also the curator of the Fleuriau museum between 1889 and 1913. He classified the foraminifera according to d'Orbigny's *Tableau méthodique* and stuck them into tin and glass-made cells. There are today 138 slides placed in three drawers (Fig. 3A) labelled "Foraminifères recueillis et determinés par d'Orbigny père" [Foraminifera collected and determined by d'Orbigny's father]. The specimens that have not been mounted are kept in 36 glass tubes identified by the samples origin (Fig. 3B) with labels mentioning "A.

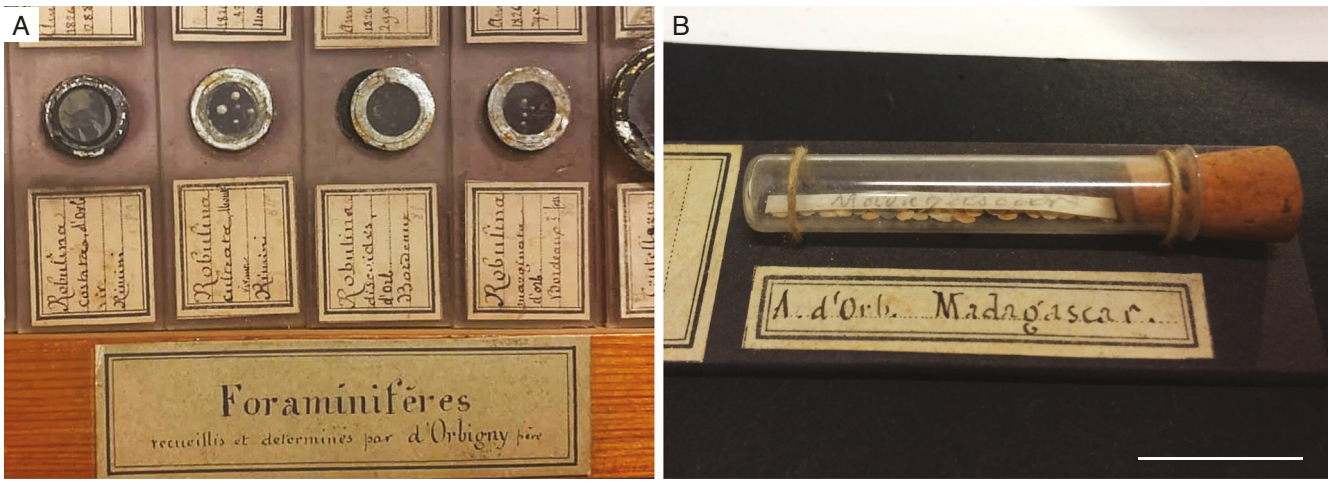


Fig. 3. — Two types of storage used for d'Orbigny's foraminifera collection at La Rochelle. At the end of the XIXth century, Charles Basset, a micropalaeontologist enthusiast, remounted some of the foraminifera that remained at La Rochelle using glass slides with tin cells and wax (**A**). Only a few tubes, labelled as "A. d'Orb." kept their original mounting (**B**). These tubes are similar with those used by Terquem for the Paris collection housed at the MNHN. Scale bar: B, 2 cm. Photos: C. Hairie.

d'Orb." in reference to Alcide d'Orbigny who trained on these foraminifera alongside his father (Hairie *et al.* 2022).

For years, this collection has been stored in the attics of the Museum of Natural History of La Rochelle, with uncontrolled temperature and moisture variations[1]. In the 2000s, the museum was renovated and the d'Orbigny collection was transferred into dedicated storerooms.

Scope of this study

The present work was undertaken to assess the current condition of the d'Orbigny foraminifera collection housed at the MNHN and evaluate the causes and progress of Byne's decay. The approach combines visual observation of pictures of specimens, chemical analyses and compilation of historical accounts, for a better understanding of the main cause of the observed alterations.

Pictures of the foraminifera, taken in 2016 within the E-Récolnat project, will be considered to evaluate and quantify the different types of damage. Correlations between the damage and the foraminifera intrinsic properties (hyaline, porcelaneous, fossil, recent) will be researched, using a statistical approach if necessary. To estimate if the decay is still active, the 2016 pictures will be compared to photographs taken in the 1940s. This assessment will be propitiously completed by micro-Raman analyses for a non-invasive chemical identification of occurring crystalline phases.

As environmental conditions are key parameters of Byne's decay, it was found important to briefly recall the history of the collection and discuss the different environments where it was housed at the MNHN (the reader is referred to Hairie *et al.* 2022 for thorough details). It was also found relevant to compare the current condition of the Paris specimens with the condition of similar specimens also collected by d'Orbigny, yet preserved in a totally different environment at the Museum of La Rochelle, France.

MATERIAL AND METHODS

Visual assessment of the collections' conditions

Considered specimens and pictures

After d'Orbigny's death, the inventory of the foraminifera collection donated to the MNHN was entrusted to the naturalist assistant Hyppolite Huppé. It was finished in 1860 and mentions 4100 specimens (Hairie *et al.* 2022). Yet, within 150 years of history, some of them have disappeared, which led us to consider, for our conservation report: 1) the foraminifera that were photographed during the 2016 E-Récolnat campaign (3594 specimens); and 2) the grade E foraminifera (27 specimens, not photographed because they were too highly damaged). This represents a total of 3621 specimens. For information, the digitization of the collection was realized with a Leica 165C magnifier and a high-definition digital camera, combined with Leica Application Suite image processing software for 3D objects. All the E-Récolnat pictures shared in this article are available in the MNHN Database. In the present work, we will use the original names of the species given by d'Orbigny, as they appear on the cardboard support to which the tubes containing the foraminifera are glued. This is to facilitate the identification with the specimens studied, respecting the MNHN inventory numbers of the collection.

During the E-Récolnat campaign, it was observed that the inner side of the glass tubes had an oily aspect, some of them displaying small droplets (Fig. 1C). This change of aspect was first interpreted as water condensation. It was therefore decided to remove all remaining cotton and cork caps to let the tubes dry. The droplets turned into small crystals, thus echoing the salt efflorescence observed on the specimens. These crystals are also investigated in this work.

Furthermore, to verify if the development of Byne's decay was specific of the MNHN storage, we undertook the condition report of the foraminifera housed at the Museum of La Rochelle in April 2021. This report was performed with UV-visible Dino-Lite digital microscopes and DinoCapture2.0 software.

Criteria selected for the visual assessment

To assess the extent of the damage, it was decided to make a condition report as precisely as possible. Evidence of crystalline growths was first sought. They sometimes correspond to tiny spots that could easily go unnoticed on specimen in "fair" conditions (Fig. 4, specimen B1). More often, they take the appearance of small crystals scattered over the test (Fig. 4, specimen B2). When these crystals are more numerous, it becomes more difficult to recognize the foraminifer (Fig. 4, specimen C2). Sometimes they entirely cover the test and make it appear as a "snowball" (Fig. 4, specimen D2). Most of these crystals are white (Fig. 4, specimens B2, C2, C4, D1, D2), but some of them tend to be transparent (Fig. 4, specimens B3, B4, C1, D3).

Structural damage is another important feature in this report. The most obvious type of damage corresponds to cracks. Two types of cracks were defined: cracks obviously provoked by crystalline growth behind the surface of the test (Fig. 4, specimens C1, C4, D1) and cracks that might have been caused by other reasons, such as inappropriate handling or glue drying (Fig. 4, specimens B5, D5). To dissociate Byne's decay damage from the other reasons in this condition report, only cracks that seem uncorrelated with the salt formation were taken into consideration as "cracks".

Another, less obvious structural damage was also defined as a sort of chemical dissolution of the test, which seems to lose its texture (Fig. 4, specimens B3, C3) and becomes more or less equally transparent (Fig. 4, specimens C3, C5). The specimen is then significantly more fragile and breaks easily in protruding areas, as if the test was partially affected by dissolution (Fig. 4, specimens C5, D4). This type of alteration was thus referred to as "dissolution". This dissolution also goes with some additional re-crystallisation on part of the test, which suggest the presence of dissolution-recrystallisation processes (i.e. the matter lost by the specimen recrystallized further away) (Fig. 4, specimens B3, C3).

Unusual colours are also observed on some foraminifera. The most common corresponds to an orange-brown hue appearing unevenly on the test (Fig. 4, specimens C4, D4). This colouring may be due to diagenetic process (e.g. formation of manganese or iron-rich crusts on fossil specimens; Glock *et al.* 2012; Chen *et al.* 2021) but could also be linked to some degradation occurring in the Museum environment. Whether it was or not present initially on the foraminifera remains an open question. Pending further investigation to separate natural and diagenetic colours from Byne's decay, we recorded all the specimens showing these colour variations as "orange colouring".

Finally, the specimens were ranked from grade A to E according to the amount of their damage (Fig. 4). Grade A corresponds to the specimens in fair condition with no alteration or, in a few cases, small questionable alterations. Grade B indicates that the specimen is slightly damaged, and that the species to which it belongs remains clearly recognizable. Grade C corresponds to higher damage that obstructs the legibility of the species, such as clusters of crystalline growths or structural damage. Grade D refers to foraminifera that are no more recognizable because of the damage. Grade E corresponds to few foraminifera that were not photographed during the E-Récolnat campaign due to their poor condition (i.e. it was estimated there was nothing left to digitized). Therefore, D and E correspond to the highest grades of the decay, that we will merge as "D+E".

A statistical approach to consider the intrinsic characteristics of the specimens

It was found interesting to evaluate the impact of the foraminifera intrinsic characteristics on the development of Byne's decay with a statistical approach. The first characteristic deals with the hyaline or porcelaneous nature of the test that was relatively easy to define according to the names of the species. A total of 1397 hyaline and 582 porcelaneous specimens have been identified and these numbers were found large enough to implement a statistical treatment. A second feature interesting to explore concerns the benthic/planktonic mode of life of the specimens. Yet, the d'Orbigny collection mostly deals with benthic specimens, which makes this criterium difficult to evaluate with a statistical approach.

The age of the specimens was also considered, although it could not be precisely defined. Indeed, many of the localities mentioned in the inventory clarified whether the specimens were sampled from recent or fossil deposits. For instance, foraminifera sampled in a country that has no access to the sea, such as Austria, obviously correspond to fossil samples. Those coming from countries having access to the sea are more problematic. Fortunately, d'Orbigny made a clear distinction between fossil and recent foraminifera in his classification: he listed the species of foraminifera sampled from coast sand (e.g. Cuba, Canary Islands, Madagascar, Red Sea, Adriatic Sea, etc.) as "vivant", the French equivalent of "living" (d'Orbigny 1839: 46, table XLVI). Therefore, the geographical locations identified in the micropalaeontology inventory made it possible to define two groups. The first, hereafter named as recent, gathers 743 specimens. They were collected at sea in coastal-offshore environments and were also living, recently dead or subrecent. The second group hereafter named as fossil, gathers 1113 foraminifera collected from continental outcrops, such as the Vienna Basin and Paris Basin. These two groups were considered large enough to develop a statistical approach. The main difference between these two groups is that recent foraminifera have not undergone diagenesis or only low levels of diagenesis, whereas fossil foraminifera have undergone some degree of diagenetic processes such as dissolution and recrystallisation during the burial of sediments.

To evaluate the impact of each feature (hyalin/porcelaneous, recent/fossil) on the development of Byne's decay, it was decided to run a Chi-square test with Excel. This statistical hypothesis test is used to examine whether two categorical variables are independent. A null hypothesis H0 must be defined, in our case: "the occurrence of Byne's decay is not influenced by the tested intrinsic feature". The results of the test will give a chi-square (chi^2) value and a probability p. The smaller the p-value, the lower the probability of making an error by rejecting H0. With a significance level (α) of 5% and

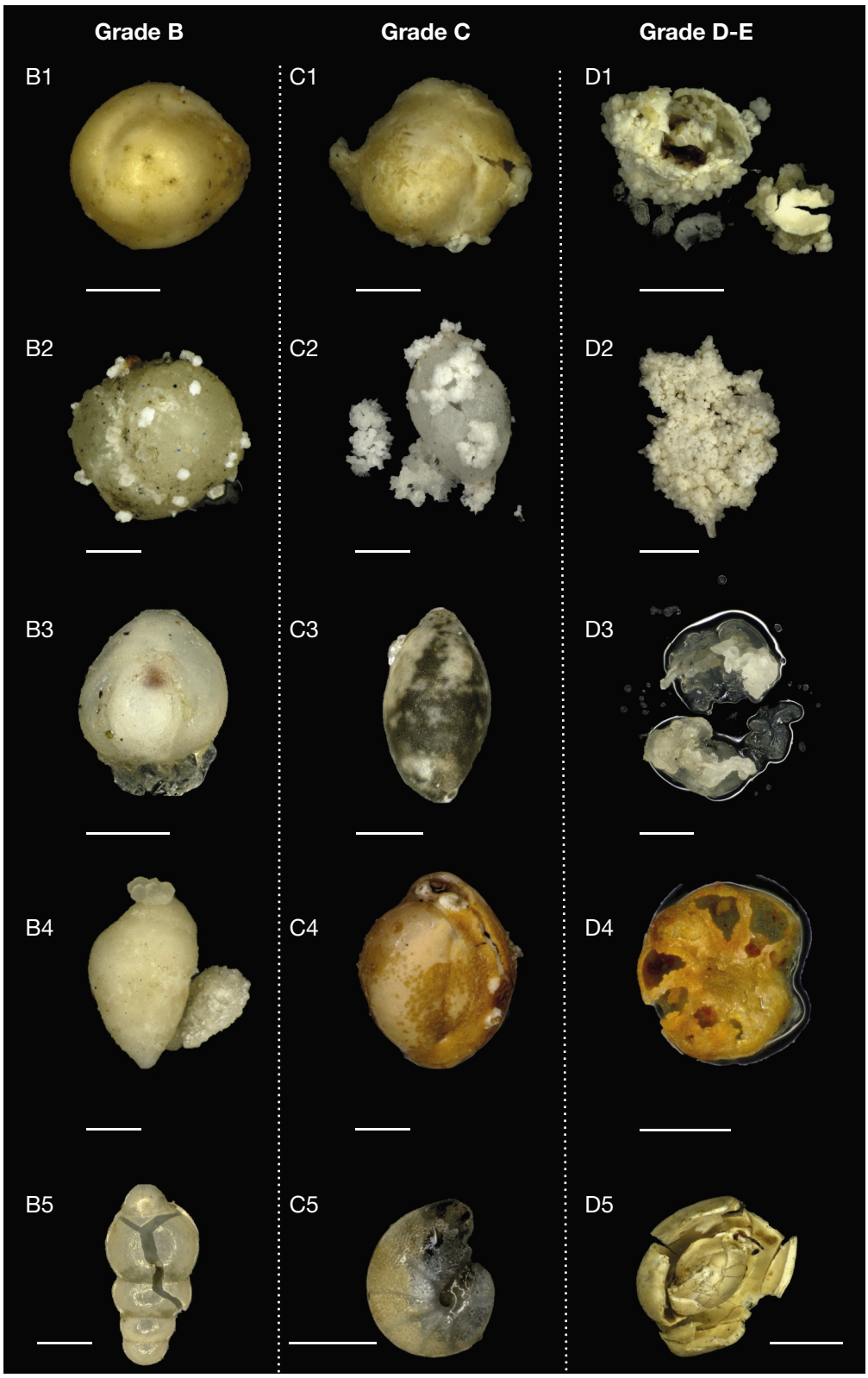


FIG. 4. — Variety of the damage observed on foraminifera from the d'Orbigny collection housed at the MNHN, Paris. Inventory references of the mountings: **B1**, MNHN.F.FO414-10, *Triloculina cryptella* d'Orbigny, 1839 (hyaline, recent); **B2**, MNHN.F.FO824-14, *Globigerina elevata* d'Orbigny, 1840 (hyaline, fossil); **B3**, MNHN.F.FO61-10, *Globulina irregularis* d'Orbigny, 1846 (hyaline, fossil); **B4**, MNHN.F.FO734-14, *Bulimina obliqua* d'Orbigny, 1840 (hyaline, fossil); **B5**, MNHN.F.FO48-11, *Dimorphina obliqua* d'Orbigny, 1846 (hyaline, fossil); **C1**, MNHN.F.FO414-12, *Triloculina cryptella* d'Orbigny, 1839 (hyaline, recent); **C2**, MNHN.F.FO14-17, *Bulimina ovata* d'Orbigny, 1846 (hyaline, fossil); **C3**, MNHN.F.FO822-11, *Glandulina laevigata* (d'Orbigny, 1826) (hyaline, origin unknown); **C4**, MNHN.F.FO638-14, *Triloculina unidentata* d'Orbigny, 1826 (Porcelaneous, origin unknown); **C5**, MNHN.F.FO478-11, *Nonionina umbilicata* d'Orbigny, 1826 (hyaline, fossil); **D1**, MNHN.F.FO414-13, *Triloculina cryptella* d'Orbigny, 1839 (hyaline, recent); **D2**, MNHN.F.FO236.2-10, *Calcarina calcar* d'Orbigny, 1830 (hyaline, recent); **D3**, MNHN.F.FO230.1-10, *Biloculina carinata* d'Orbigny, 1839 (porcelaneous, recent); **D4**, MNHN.F.FO510-19, *Rotalia siennensis* d'Orbigny, 1826 (hyaline, fossil); **D5**, MNHN.F.FO399-17, *Quinqueloculina magellanica* d'Orbigny, 1839 (porcelaneous, recent). Scale bars: B, C, D3, D4, 0.2 mm; D1, D2, D5, 0.5 mm. By C. Hairie (plate), photos from Récolnat.

a degree of freedom (DL) of 1, the table of chi-square values gives a critical value of 3.841. If the calculated chi-square value is below this critical value, there is no significant difference between the variables and the null hypothesis H0 is retained. On the opposite, if the calculated chi-square value is higher than the critical value, there is a significant difference between the variables and H0 is rejected. In our case, the rejection of H0 would mean the tested feature of the specimens does have an influence on Byne's decay.

Comparison with Lys' micropalaeontology file

Maurice Lys was an engineer working at the Institut français du Pétrole, a French research institute dedicated to oil industry. He worked on the d'Orbigny's foraminifera collection in the years 1945-46, and established about 800 index cards, sorted alphabetically, of the different species determined by d'Orbigny (Lys 1947). Most of the cards are illustrated with photographs of one or several specimens, chosen among Terquem's preparations. These photographs constitute a valuable documentation of the condition of the MNHN foraminifera in the middle of the XXth century. Their original purpose was to illustrate the species, but they can also be used today to get some information on the development of the degradation.

We also attempted to compare Maurice Lys' photographs with the 2016 E-Récolnat pictures to point out a possible progression of the degradation over the last 70 years. This could not be done on the whole collection as Lys did not photograph all the specimens, but only a few representatives that probably were the best-looking ones. Moreover, the high number of foraminifera in some preparations did not facilitate the identification of the specimen that was photographed. In this context, we were able to make a connection between the 1940s and 2010s photographs for 137 specimens.

Chemical analysis

Chosen specimens for the chemical analysis

Because it was not possible to analyse all damaged specimens in the MNHN collection, only 28 preparations showing different types of efflorescence (white, transparent or orange-coloured crystals) were selected for chemical analyses. Most of these specimens were grade D, with varying compositions (hyaline/porcelaneous) and age (fossil/recent). It constituted a corpus of 66 specimens.

Reference samples

As Raman spectra of calcium organic salts are not always easily accessible, reference samples were prepared and, when necessary, their crystalline structure was confirmed by powder X-ray Diffraction analysis (PXRD), using a D2-Phaser equipment (Bruker). Some of them corresponded to commercial products. Some others were synthetized in laboratory conditions, following published protocols (Tennent & Baird 1985; Bette *et al.* 2019). Finally, only a limited number of reference samples appeared useful for the present work. They correspond to: 1) magnesium formate dihydrate (Ref 00793-100G-F Sigma-Aldrich); 2) calcium lactate pentahydrate (Ref 21185-250G-F Sigma-Aldrich); 3) orthorhombic calcium formate α-$Ca(HCO_2)_2$ (Ref 21134-250G-F Sigma-Aldrich); 4) anhydrous sodium formate phase II (Ref 71539-500G Sigma-Aldrich); and 5) tetragonal calcium formate ß-$Ca(HCO_2)_2$, also referred to as "Formicaite". This latter was synthetized in laboratory conditions by heating the orthorhombic calcium formate phase at 400°C for 2 hours. After cooling, the resulting product was kept at 0% RH (= Relative Humidity) to insure its stability (Schutte & Buijs 1964; Mentzen 1971).

Raman spectrometry

Because of the fragility, small size and patrimonial value of the specimens, sampling was excluded. Analyses had to be performed in-situ, in a non-destructive and non-invasive way. To this respect, micro-Raman spectrometry appears as an appropriate tool allowing local analyses of spots of a few square microns as well as the speciation of both mineralogical and organic phases (Nasdala *et al.* 2004; Rouchon *et al.* 2012; Pasteris & Beyssac 2020). Analyses were conducted on a micro-spectrometer (InVia, Renishaw) equipped with a 785 nm laser beam and using a magnifier ×50. Despite some fluorescence of the matrices, a reasonable signal was obtained using 1-10% of the intensity of the beam. Three to 12 spectra were collected on each specimen depending on the amount of crystals and homogeneity of signatures. No change in the spectra was observed during acquisition and no damage was visible on the samples during and after exposure.

Spectra were collected with the WIRE acquisition software from Renishaw. The OMNIC software of Thermo Fisher Scientific was also used to plot the data as it enables more easily comparisons between a large number of spectra.

Scanning Electron Microscopy (SEM)

To describe the morphologies of crystalline growths at the micrometric and nanometric scales, the foraminifera were analysed with a SEM imaging system equipped with an Energy-dispersive X-ray microprobe (VEGAII, TESCAN). Yet this technique necessitates an exposure to relatively high vacuum conditions, which represents an additional threat for the fragilized specimens. It was therefore decided to progressively decrease the pressure down to a value of 12 Pa. Such caution proved to be sufficient to ensure the stability of the foraminifera during the analyses while providing satisfactory images.

The backscattered electrons (BSE) mode, with accelerating voltage of 15 kV, was chosen to highlight the chemical contrast at the surface of the foraminifera. In such conditions, areas containing heavy elements appear light grey to bright white on BSE images while those containing lighter elements are darker. This enables the distinction of different degradation phases. Energy-dispersive X-ray spectroscopy (EDX) was then used to identify the elements present in a selected area. This technique is able to detect a range of elements (basically all elements heavier than sodium), and thus appropriate to distinguish between calcium salts and other salts.

TABLE 1. — Overview of the condition report of d'Orbigny's foraminifera collection. Byne's decay is considered as occurring certainly when there is obvious crystalline growth. It is probably occurring when different unusual features, such as dissolution phenomena, are observed (see part:"Crystalline growth, but not only..."). Percentages are calculated in relation to the total number of specimens. Abbreviations: **Nb**, Number; **Spec.**, specimen; **prop.**, proportion; **Diss.**, dissolution; **Cracks**, presence of cracks; **White**, presence of white crystals; **Transp.**, presence of transparent crystals; **Orange colour.**, occurrence of an orange colouration of the test; **Snowball**, covered by white efflorescence with a snowball aspect; **Certain.**, certainly; **Prob.**, probably.

				among which (nb.)			among which (nb.)				Byne's decay (%)		
Grade	Nb. of spec.	Global prop.	Structural damage (%)	Diss	Cracks	Crystalline growth or colouration	White	Transp.	Orange colour.	Snow ball	Max. proport.	Certain.	Prob.
A	1396	39%	0%	0	0	4%	0	0	138	0	0%	0%	0%
B	1199	33%	14%	252	254	27%	834	49	182	0	30%	21%	9%
C	582	16%	14%	210	139	14%	381	85	106	31	16%	12%	4%
D + E	444	12%	12%	48	23	12%	259	129	29	80	12%	12%	1%
Total Nbr.	3621	–	–	510	416	–	1474	263	455	111	–	–	–
%	–	100%	40%	14%	12%	57%	41%	7%	13%	3%	59%	45%	14%

The main limitation of these elemental analyses approach lies in the fact that the foraminifera are stuck on a soda-lime glass slide. This type of glass contains elements that may also be present in the specimen's composition (sodium, calcium, etc.) When the signal corresponding to an element is relatively low, it is sometime difficult to assess its origin (foraminifer, degradation product or glass slide). For this reason, no elemental quantification was attempted and only the strongest X-ray peaks were taken into consideration for elemental characterization.

CHECKING THE CONDITIONING MATERIALS AND THE CLIMATE

A previous work, focused on the MNHN collection, enabled to identify the numerous locations of d'Orbigny's collection since its acquisition by the Museum (Hairie *et al.* 2022). Archival records were consulted again to evaluate in detail the different environmental conditions the collection may have endured. It is important to note that the current palaeontology gallery in which the collection stayed for a while has undergone only limited renovation and is not equipped with modern air-conditioning. Therefore, it was found relevant to complete historical reports by some data provided by the dataloggers placed in the current Gallery (Hanwell temperature and humidity wireless system) and in the current storage building (iButton, DS1923, Proges Plus).

Another approach was carried out to evaluate the emission of VOCs from the storage materials used by Terquem in the mountings. Reactive AD-strips (Image Permanence Institute, Rochester, USA) were used as colour indicators. These dye-coated paper strips are designed to detect and measure acidic vapours by changing their colour from blue to yellow. They were placed in hermetic containers with 1g of each material (coton, blue paper or cork) and for the same duration of 4 days for each material. Their colour was then measured with a portable spectrophotometer Konika Minolta, based on 1976 CIELAB coordinates L*a*b* (L* lightness; a* position on the green-red axis; b* position on the blue-yellow axis). The change in colour ΔE* was then estimated according to the equation: $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$.

RESULTS

VISUAL ASSESSMENT OF THE DECAY

General results

Statistical results obtained from the condition report (Table 1) show that the collection has greatly suffered as only 39% of the foraminifera seem to be in good condition (Grade A). Yet, on most altered specimens, the damage is relatively limited as 33% of the specimens belong to grade B and can thus still be used for research. Finally, the most degraded specimens that are of no use for palaeontology studies (Grade C, 16% and Grade D + E, 12%) correspond to approximately a fourth of the collection (28%).

Table 2 shows that a great part of the collection is affected by crystalline growths or test coloration (57%). Some of these crystalline growths are transparent (7%), and most of them are white (41%). Among these, the snowball aspect that corresponds to a high level of white efflorescence, concerns only a small portion of the collection (3%). The presence of a pronounced orange-brown colour cannot be neglected since it affects a significant proportion of the foraminifera (12%), although its origin remains difficult to determine.

Another aspect of the degradation deals with structural damage that concerns 40% of the foraminifera. They sometimes appear attributable to inappropriate manipulation and independent from Byne's decay (cracks, 12% of the foraminifera). Sometimes, they are obviously related to the dissolution of the test that makes it more fragile ("dissolution", 14% of the foraminifera). Yet, in most cases, it remains difficult to assess with certitude the cause of cracks and fractures: crystalline growth? dissolution of the test? manipulation?

Crystalline growth, but not only...

The diversity of deteriorations raises questions about the type of degradations that can be attributed to Byne's decay. It is commonly acknowledged that Byne's decay provokes the development of white crystalline efflorescence at the surface -or subsurface- of calcareous items exposed to VOCs (Tennent & Baird 1985; Shelton 2008). Depending on the composition (presence of other ions) and porosity of the matrix, different crystalline

TABLE 2. — **A**, Byne's decay vs composition and age of the specimens. Percentages are calculated in relation to the number of foraminifera presenting the same feature (hyaline, porcelaneous, fossil, recent). "Fossil" refers to foraminifera sampled on a continental outcrop while "recent" refers to foraminifera sampled at sea or on the coast; **B**, Repartition of the damage grades and features observed on the specimens suffering by Byne's Decay vs composition and origin. Percentages are calculated in relation to the number of foraminifera presenting a specific feature (hyaline, porcelaneous, fossil, recent). "Fossil" refers to foraminifera sampled on a continental outcrop while "recent" refers to foraminifera sampled at sea or on the coast. Deviations of the percentages calculated within the hyaline and porcelaneous (respectively fossil and recent) populations are ranked in the middle line (respectively last line) of the table. **=**, no significant deviation (< 4%); **≈**, limited deviation (4% < x < 10%); **×**, obvious deviation (≥ 10%). Abbreviations: **Spec.**, specimen; **Diss.**, Dissolution; **Cracks**, presence of cracks; **White**, presence of white crystals; **Transp.**, presence of transparent crystals; **Orange colour.**, orange colouration of the test; **Snowball**, covered by white efflorescence with a snowball aspect.

A	Feature	Total specimens	Byne decay	Proportion	Independancy test (α = 0.05; DL = 1, critical chi² = 3.84)
Composition	Hyaline	2451	1397	57%	p = 0.00000125
	Porcelaneous	877	582	66%	chi² = 23.50: H0 rejected
Origin	Fossil	1938	1113	57%	p = 0.173
	Recent	1241	743	60%	chi² = 1.85: H0 retained

B	Degradation grades				Altered struct.	among which (nb.)		Cristal. growth or colour.	among which (nb.)			
	A	B	C	D+E		Diss	Cracks		White	Transp.	Orange colour.	Snow ball
Hyaline (1397 spec.)	1%	51%	28%	20%	67%	29%	17%	87%	61%	15%	16%	3%
Porcelaneous (582 spec.)	0%	50%	24%	26%	58%	11%	10%	96%	86%	7%	12%	12%
	=	=	≈	≈	≈	×	≈	≈	×	≈	≈	≈
Fossil (1113 spec.)	1%	59%	27%	13%	56%	22%	18%	89%	73%	8%	17%	4%
Recent (743 spec.)	0%	40%	26%	34%	72%	25%	9%	89%	61%	19%	9%	8%
	=	×	=	×	×	=	≈	=	×	×	≈	≈

phases may form, thus provoking more or less severe physical damage (Paterakis 2016). However, the fact that shells could become more transparent with a loss of texture is not mentioned in the literature on Byne's decay, probably because only macroscopic specimens were concerned (Byne 1899; Nicholls 1934; Tennent & Baird 1985; Shelton 1999, 2008). For these latter, the alteration remains rather superficial and does not significantly modify the calcareous matrix behind the surface. On the contrary, the alteration of microscopic specimens (such as foraminifera) will more rapidly concern the whole matrix, significantly modifying the internal test structure, and thus its optical properties. To define the proportion of specimens affected by Byne's decay, we thought important to distinguish two levels of assessment (Table 1): the first corresponds to obvious and visible damage certainly provoked by Byne's decay (ex: crystalline growth) while the second mostly corresponds to damage probably resulting from Byne's decay (ex: dissolution or orange colour). Taking these two levels into consideration, the proportion of d'Orbigny's foraminifera affected by Byne's decay *stricto sensu* is at least of 45%, but more probably closer to 59%. A closer look shows that these foraminifera are in majority grade B (21% to 30%), followed by grade C (12 % to 16%) and D-E (12%). Such progression suggests that Byne's decay happens gradually and does not specifically lead to the destruction of the foraminifera once it has just started. However, the proximity between the proportion of grade C and grade D-E agrees with a potential "reservoir" effect (Paterakis & Steiger 2015) below the salt overlay, that nourishes the salt formation as long as there is moisture variations and calcium carbonate available.

Influence of the nature and age of the foraminifera tests

The hyaline or porcelaneous nature of the test, which is related to different magnesium content and matrix crystallinity (de Nooijer *et al.* 2023), may have an influence on the degradation. This possibility was tested on the 2451 hyaline and 877 porcelaneous foraminifera that were identified in the collection. On this set of samples, the hyaline or porcelaneous nature of the test was crosschecked with the occurrence of Byne's decay.

Table 2A shows that hyaline specimens are affected at a proportion of 57% against 66% for porcelaneous species. The statistical Chi-square test, based on the H0 hypothesis "The proportion of specimens affected by Byne's decay is independent from the test composition", shows a low probability (p = 0.00000125), indicating that H0 can be easily rejected. Therefore, the test composition does have an influence on Byne's decay, and porcelaneous specimens appear more prone to Byne's decay than hyaline ones. The detailed distribution of the damage summarized in Table 2B shows some additional differences between these two kinds of biomineralization: dissolution phenomena are more frequent among hyaline specimens than among porcelaneous ones (29% vs 11%). Conversely, porcelaneous specimens seem more affected by crystalline development than hyaline ones (86% vs 61%).

The influence of the age of the test (recent vs fossil as depicted in part: "A statistical approach to consider the intrinsic characteristics of the specimens") was also evaluated. Here, the global proportion of fossil (57%) and recent (60%) specimens affected by Byne's decay are close (Table 2A). The Chi-square test shows a probability (p=0,17) higher than the

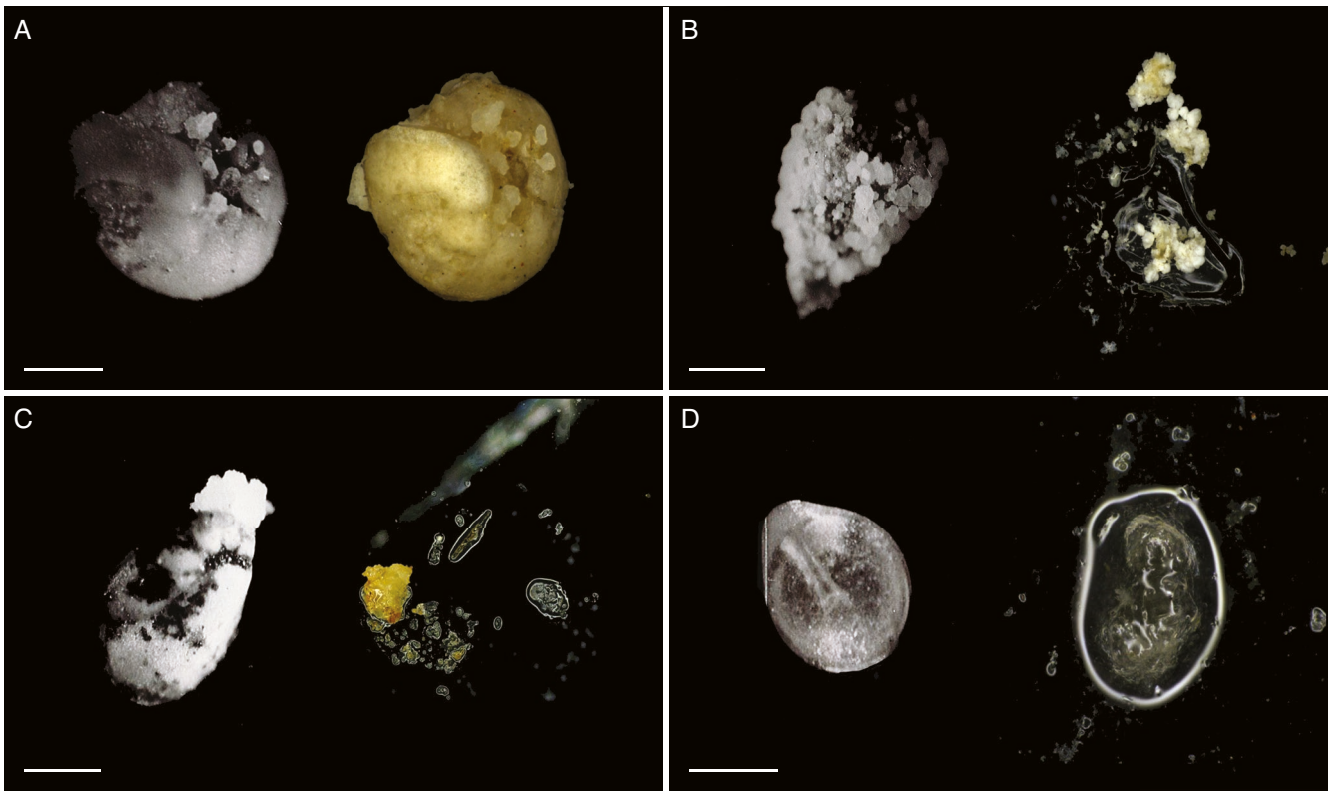


Fig. 5. — Comparison of some foraminifera condition between the 1940s (left picture) and today (right picture). A minority of foraminifera do not show additional deterioration (**A**). Yet many of them show an increase of the damage (**B**, **C**). The development of salt over specimens that were in good condition in the 1940s (**D**) confirms that degradation has continued. Inventory references of the specimens: **A**, MNHN.F.FO467-12, *Gyroidina soldanii* d'Orbigny, 1826 (hyaline, recent); **B**, MNHN.F.FO322.1-10, *Textularia candeiana* d'Orbigny, 1839 (agglutinated, recent); **C**, MNHN.F.FO.313-10, *Cancris sagra* (d'Orbigny, 1839) (hyaline, recent); **D**, MNHN.F.FO379-10, *Oolina compressa* d'Orbigny, 1839 (hyaline, recent). Scale bars: A, D, 0.2 mm; B, C, 0.5 mm. By M. Lys and Récolnat (photos) et C.Hairie (plate).

significance level of 5%. Therefore, it appears the sample age has statistically no influence on the proportion of specimens affected by Byne's decay. However, there is a significant difference in the intensity of the degradation (Table 2B). The proportion of grade B damage appears far more important for fossil specimens (sampled from on-land outcrops) than for recent ones (59% vs 40%). Conversely, the proportion of grade D+E remains limited for fossil specimens (13%), while it increases by a factor of 2 for recent ones (34%). These observations are consistent with a higher proportion of structural damage for recent foraminifera when compared to fossil ones (72% vs 56%).

Finally, even if Byne's decay has developed in relatively similar proportions within hyaline/porcelaneous, or fossil/recent specimens (Table 2A), different tendencies are observed within these different groups. The hyaline/porcelaneous nature of the test seems to influence the type of degradation (dissolution/crystallisation) while its age (fossil/recent) plays a role on the degradation rate.

Comparison with the Lys file: no fungi, but crystals

For historical palaeontology or malacology collections, regular surveys and climatic control have been rarely taken during the XXth, since most of the scientists in charge of the collections were not aware of the risk of Byne's decay. Many of them were confusing these crystalline growths with fungi (Shelton 2008). This typically happened on the d'Orbigny's foraminifera collection. In 1914, the English palaeontologist Edward Heron-Allen paid a visit to France to document d'Orbigny's work and life. He noticed that "*The types or co-types at La Rochelle* […] *are for the most part overgrown with mycelium and fungus. Several of the Paris types are also fungus-grown*" (Heron-Allen & Earland 1915). Yet, no trace of fungi development has been reported since then, and it is more probable that Heron-Allen observed the first signs of Byne's decay.

Maurice Lys' file confirms this theory since several specimens appeared already in very poor state during his time at the MNHN (Lys 1947). This document offers today a unique opportunity to estimate if there has been some evolution of the decay between 1940 and 2016, which was possible for a total of 137 specimens. On 67 of them, that also correspond to slightly damaged specimens (grade B), no change was noticeable between 1947 and 2016 (Fig. 5A). However, for the other 70 specimens, an obvious spreading of the salts is observed with a significant deterioration of the test (Figs 5B-C). Most of these specimens were already deeply damaged in the 1940s (grade C and D) which agrees with the presence of a "reservoir effect" for altered specimens. Some were also in good condition in 1947, but are today totally destroyed (Fig. 5D). These observations highlight that the decay started long before the 1940s and was still running on between 1940 and 2016.

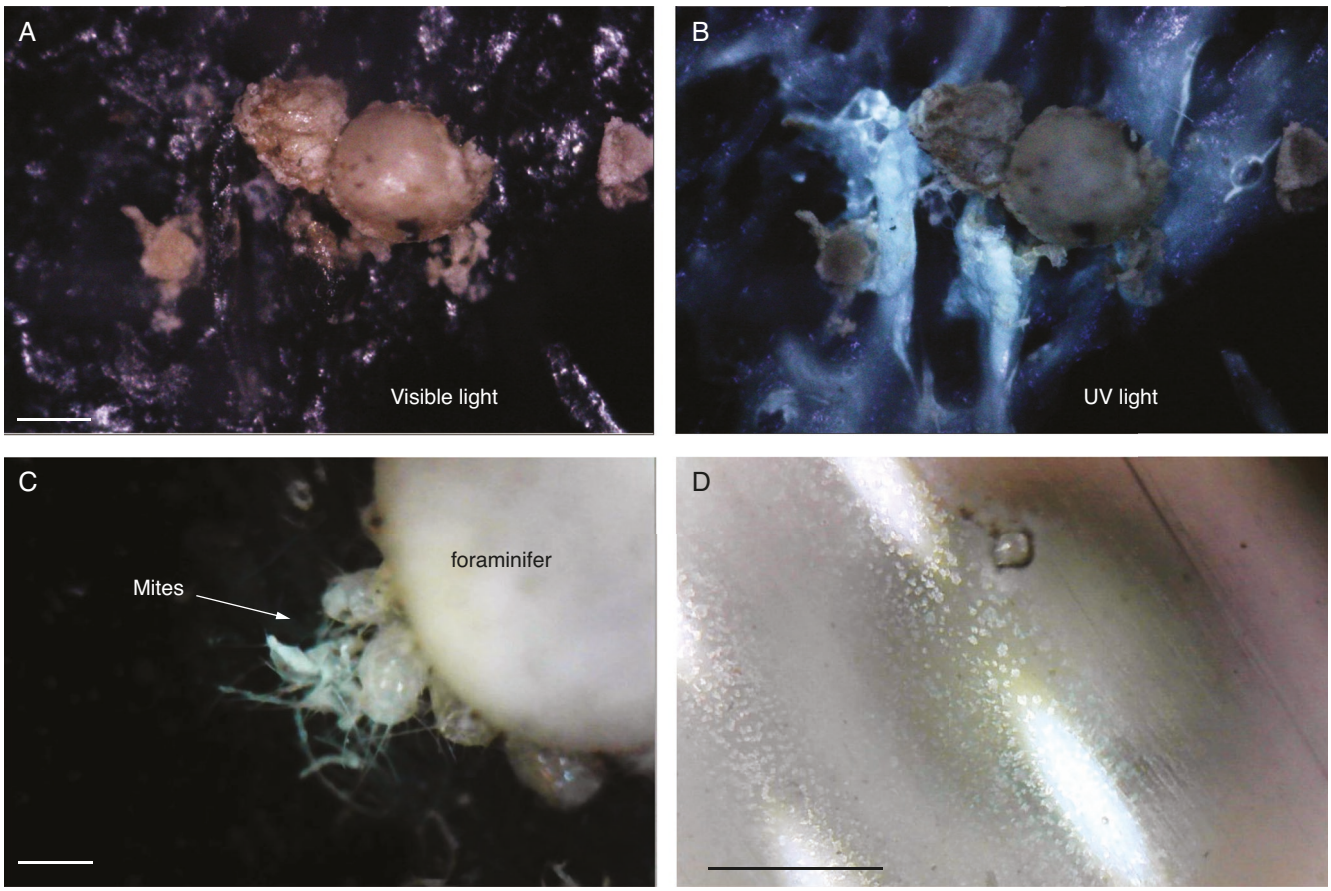


Fig. 6. — Damage observed on the d'Orbigny collection housed at the Museum of La Rochelle: **A**-**C**, mountings represented Fig. 3A; **D**, tubes containing the well-preserved foraminifera illustrated on Fig. 3B. On the mountings, crystalline growth is sometimes observed on the foraminifers (**A**) that are embedded in a UV fluorescent glue (**B**). The abusive use of glue in Basset's mountings attracted insects inside the mountings, including white mite (**C**) that can be found next to some foraminifera. Even if d'Orbigny's original tubes are far better preserved, we were able to spot some glass alteration inside the tubes (**D**). Yet it is much less developed than what can be seen on the Paris collection. References of the mountings: **A**, MHNLR.T1.C2.L1, *Polymorphina dilatata* d'Orbigny, 1826 (hyaline, fossil); **B**, **C**, MHNLR.T1.C3.L12, *Textularia gibbosa* d'Orbigny, 1826 (agglutinated, recent); **D**, MHNLR.T4.C1.L14, sediment from Bourbon (Réunion). Scale bars: A-C, 0.2 mm; D, 2 mm. Photos: C. Hairie.

Comparison with La Rochelle

Among the three drawers housed at the Museum of La Rochelle, eight slides display damage that could be attributed to Byne's decay (Fig. 6A) and nine are empty. The number of damaged foraminifera was estimated about 20 over 304, corresponding to approximately 7% of the collection. This proportion is significantly lower than that of the Paris collection, which ranges from 45% to 59%. The different storage conditions in the Museum of La Rochelle, in terms of material and environmental parameters (T and RH), could explain this difference. However, this does not mean that the La Rochelle collection is in good condition: all mountings are rather dirty and half of them show structural damage, sometimes with missing glass. Numerous arthropods cadavers can also be observed alongside the specimens (Fig. 6C). The glue used to stick the foraminifera is UV-fluorescent and therefore probably made of gelatine. Contrary to the Paris mountings on which no obvious trace of adhesive was visible, the mountings that are attributed to Basset show large amounts of glue, sometimes embedding the foraminifera. Many of the foraminifera thus show damage that seem to be linked with this excessive use of glue (Fig. 6B): their surface structure seems eroded (dissolution) and they are difficult to recognise. When taking such degradations into consideration, the number of damaged foraminifera in Basset's drawers goes up to 137 and corresponds to 45% of damaged specimens, a proportion closer to the foraminifera housed in Paris.

In contrast, the original tubes containing d'Orbigny's material, placed in the last drawer (Fig. 3B), appear in excellent condition. Foraminifera inside do not show any trace of salts or dissolution. However, a trained look reveals some start of chemical deterioration of the glass inner surface (Fig. 6D). This slight damage corresponds to an early stage of glass degradation and recalls to a lesser extent the glass alteration observed in the Paris collection.

Considering these four drawers were kept together in the same environment for more than a century, the differences observed between Basset's mountings and d'Orbigny's original tubes clearly highlight the deleterious influence of the glue in the conservation of the foraminifera.

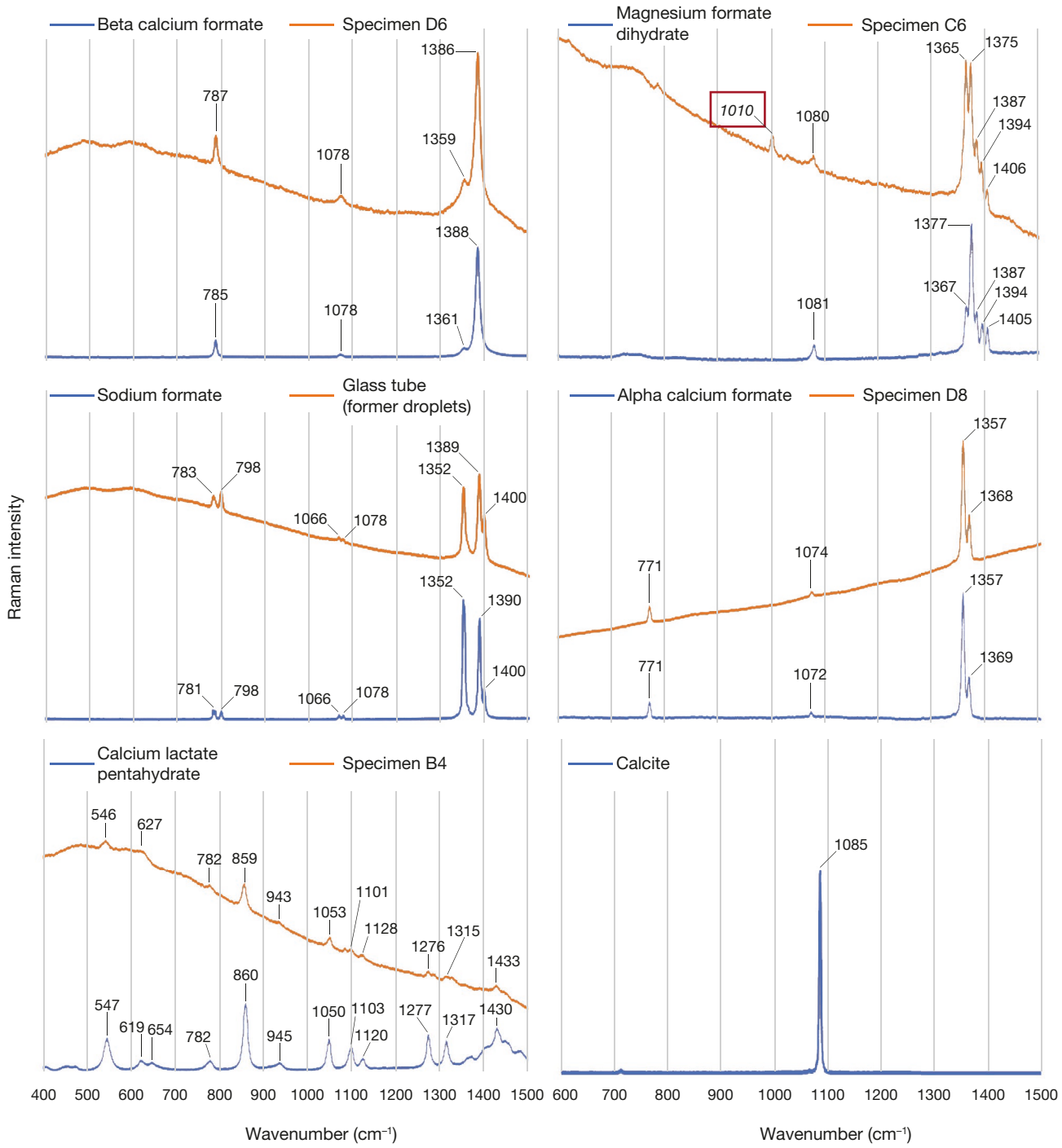


FIG. 7. — Raman spectra of model compounds and degradation products identified on the d'Orbigny's collection. Reference spectra (in **blue**) recorded on model samples provided by Aldrich or synthetized in laboratory conditions and some of the spectra (in **orange**) recorded on the specimens shown on Fig. 4. On the top left, β-calcium formate [β-$Ca(HCOO)_2$] (tetragonal) identified on the majority on damaged specimens, among which D6. On the top right, magnesium formate dihydrate [$Mg(HCOO)_2{\cdot}2H_2O$], also detected on specimen C6 (the band at 1010 cm^{-1} is exogenous and probably corresponds to calcium sulfate). On the middle left, α-calcium formate [α-$Ca(HCOO)_2$] (orthogonal) also detected on specimen D8. On the middle right, sodium formate, phase II (NaHCOO II) developed on the inner surface of the glass tubes. On the bottom left, calcium lactate pentahydrate [$Ca(CH_3\text{-}CH\text{-}OH\text{-}COO)_2{\cdot}5H_2O$], also detected on specimen B4. On the bottom right, calcite, the main constituent of the tests. We can observe fluorescence phenomena (the signal goes up or down) on the Raman spectra, that made sometimes difficult the identification of the peaks.

IDENTIFICATION OF DEGRADATION BY-PRODUCTS

Identification of the polymorphic reference phases of calcium formate

Calcium salts obtained from the crystallized mixtures were identified by XRD and characterized by Raman spectrometry, leading to the determination of reference Raman signatures that are recalled in Fig. 7 (Blue spectra). These signatures are consistent with the literature (Tennent & Baird 1985; Bette *et al.* 2019).

The Raman spectrum of the beta polymorph of calcium formate, which was not available at the beginning of this

study, was characterized in the same way. It is consistent with the recent characterisation of "formicaite" (its mineral form) that was meanwhile published (Chukanov *et al.* 2021). It shows a strong C-H in-plane bending band at 1387 cm^{-1}, a medium C-O stretching band at 1360 cm^{-1}, a weak C-H out-of-plane bending band at 1078 cm^{-1} and a medium O-C-O bending band at 786 cm^{-1}. Alpha calcium formate has a different signature (Ito & Bernstein 1956; Krishnan & Ramanujam 1973) with emission peaks at 1400 and 1390 cm^{-1} (in-plan C-H bending), 1352 cm^{-1} (C-O stretching), 1066 and 1078 cm^{-1} (out of plan C-H bending), 783 and 798 cm^{-1} (O-C-O bending) (Fig. 7). Raman spectroscopy is thus an appropriate tool for the speciation of these two polymorphs.

Analysis of the crystallized salts on damaged foraminifera

Table 3 lists the 66 analysed foraminifera (see part: "Chosen specimens for the chemical analysis") as well as the different crystalline phases that could be identified on them by Raman spectroscopy. High-resolution SEM pictures of the most characteristic phases are shown in Fig. 8. It clearly appears that the alterations could not be attributed to the growth of a single phase. However, most of the spectra correspond to two polymorphs of anhydrous calcium formate, the orthorhombic α-$Ca(HCOO)_2$ and the tetragonal β-$Ca(HCOO)_2$, with a large predominance of the latter that was detected on 42 specimens over 66.

This tetragonal β-calcium formate usually appears as bright white. The snowball aspect of some foraminifera such as those of Fig. 4 (specimen D2) or Fig. 8 (specimen D6), is exclusively related to it. β-calcium formate grows in an acicular to dendritic way with a typical multi-branching tree-like shape that happens to be more or less bulky depending on the specimens. When observed under high magnification, its final morphology evoques of a cauliflower (Fig. 8, specimen D6). In some rare cases, it also takes the form of a sphere with small holes (Fig. 8, specimen C6). The orthorhombic α-calcium formate is also present, yet in much lesser amounts as it was detected on 12 specimens. It shows a completely different morphology, with lenticular crystals grouped in a rose-like pattern (Fig. 8, specimen D8).

Some occurrences of magnesium formate dihydrate $Mg(HCOO)_2{\cdot}2H_2O$ are observed, which could be expected since foraminifera tests may contain varying proportions of magnesium depending on the species and environment. It is never observed alone but is always combined with calcium formate phases. As magnesium is lighter than calcium, crystalline growths of magnesium formate often correspond to darker areas on SEM images (Fig. 8, specimen D7). Magnesium is sometimes noticed underlying β-calcium formate crystals. It has a white aspect under the binocular and grows with dendritic structure, sometimes directly on the glass slide (Fig. 8, specimens C6). Unexpectedly, calcium lactate pentahydrate [$Ca(CH_3CH\text{-}OH\text{-}COO)_2{\cdot}5H_2O$] was detected on two specimens, where it does not cover the surface of the test but corresponds to dendritic to acicular crystals that had grown adjacent to it (Fig. 8, specimen B4). Its origin remains unexplained.

Surprisingly, no acetate or mixed formate-acetate salts were detected. We initially supposed that these salts were not observed because they had grown in the inner part of the foraminifera that is not accessible by Raman spectroscopy. This was not the case. The inner parts of the most severely damaged and broken specimens that were accessible for analyses (Ex. specimen D1 of Fig. 5) did not point out any calcium acetates but merely calcium formates and mostly the tetragonal phase [ß-$Ca(HCOO)_2$]. This "non-detection" of calcium acetate does not necessarily mean "absence" as the Raman signal was sometimes completely jeopardized by the fluorescence of the glass slide and of possible rests of clayey sediment in the test. Yet it means that these phases, if present, remain minor degradation by-products comparatively to calcium formates.

Characterization of the "droplets" inside the glass tubes

The laser beam of the Raman spectrometer was focused on the crystals that had formed inside the tubes, through the glass wall (Fig. 1C). The signature shown in Fig. 7 - Glass tube was obtained on the tube of specimen MNHN.F.FO774 *Faujasina carinata* d'Orbigny, 1839 (hyaline, fossil) which is badly affected by Byne's decay (Table 3). The spectrum shows strong Raman peaks at 1357 cm^{-1} and 1368 cm^{-1} and additional minor peaks at 1074 and 771 cm^{-1}, which are consistent with the phase II of anhydrous sodium formate (NaHCOO) that is stable at room temperature (Tajima *et al.* 1981; Heyns 1986; Heyns *et al.* 1988). This compound was also identified in previous studies as a corrosion product appearing on XIXth century glass artefacts (Robinet *et al.* 2004). This presence of sodium formate on the inner surface of glass tubes is congruent with the development of calcium formate on the foraminifera and confirms occurrence of formic acid inside the tubes.

Assessing environmental conditions at the MNHN

To better understand the current condition of the MNHN collection, it was found necessary to investigate the different environments to which it has been subjected since its donation to the MNHN in 1857. This implies considering both the micro-environment of the foraminifera (corresponding to the atmosphere inside the mountings), and the environmental conditions of the places where the collection was stored. The consultation of archival records showed that the collection's many moves are linked to the tumultuous history of the palaeontology laboratory, created at the same period. It enabled to recount the most probable locations of the collection within the institution (Hairie *et al.* 2022). In what follows, we intend to account which environmental conditions these different places may have offered. Some of them have disappeared, meaning that the only source of information lies in the MNHN archives. Some others have not significantly changed much, thus allowing environmental measurements to complete this information. The main outcome of these investigations can be found in Table 4.

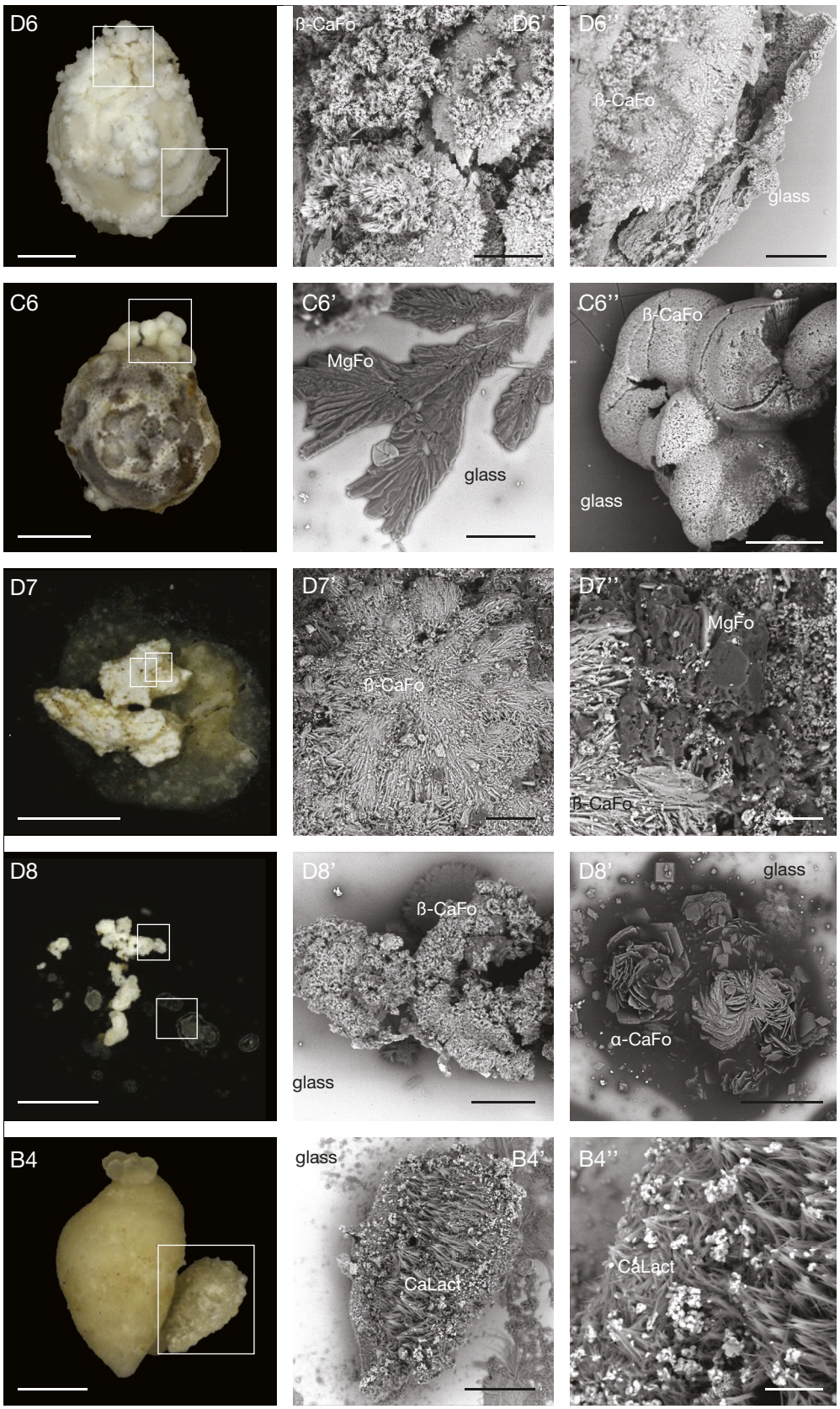


FIG. 8. — Crystalline growths observed via SEM imaging. Different morphologies are observed depending on the chemical composition of the crystals: dendritic crystals for β-calcium formate (β-CaFo) and magnesium formate (MgFo), acicular crystals for calcium lactate (CaLact), and lenticular crystals for α-calcium formate (α-CaFo). Inventory references of the specimens: **D6**, MNHN.F.FO12-11; **C6**, MNHN.F.FO626-12; **D7**, MNHN.F.FO268-10; **D8**, MNHN.F.FO297.1-10; **B4**, MNHN.F.FO734-14. Complementary information concerning the species, nature of the test or sampling location are available in Table 3. Scale bars: B4, C6, D6, 0.2 mm; D7, 1 mm; D8, 0.5 mm; B4', D8'', 100 µm; B4'', D7'', 20 µm; C6', C6'', D6', D6'', D7', D8', 50 µm. Photos, Récolnat; images MEB, C. Hairie.

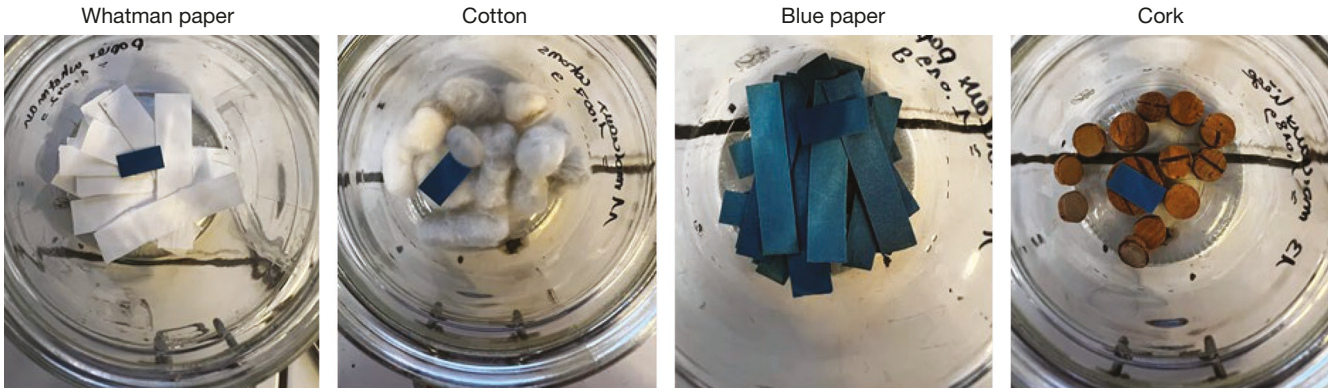
TABLE 3. — Raman analyses performed on a selection of d'Orbigny's foraminifera. Each line refers to a preparation and some of them include several specimens that were all suffering Byne's decay. The rank indicates the level of alteration. Other numbers correspond to the number of specimens on which a specific chemical species was detected by Raman spectroscopy. "Fossil" refers to foraminifera sampled on a continental outcrop while "recent" refers to recent and sub-recent foraminifera sampled at sea or on the coast. Abbreviations: **Ref.**, inventory reference of the preparation; **Nb of spec.**, number of specimens in the preparation; **β**-CaFo, occurrence of β-calcium formate; **α**-CaFo, occurrence of α-calcium formate; MgFo, occurrence of magnesium formate; **CaLact**, occurrence of calcium lactate. Taxon authorships: see Text.

Specimen number	Species	Composition	Nb. of spec.	Origin	Origin	Rank	efflorescence (effl.) type(s)	β-CaFo	α-CaFo	Ca Lact	MgFo
MNHN.F.FO12	*Biloculina affinis*	Porcelaneous	2	Austria	Fossil	D	White effl.-snowball	2			
MNHN.F.FO19	*Critelaria arcuata*	Hyaline	1	Austria	Fossil	D	White effl.	1			
MNHN.F.FO70	*Anomalina rotula*	Hyaline	1	n.a.	n.a.	D	White effl. and orange colour	1			
MNHN.F.FO93	*Nonionina bulloide*	Hyaline	1	Austria	Fossil	D	White and orange effl.		1		
MNHN.F.FO141	*Quinqueloculina juleana*	Porcelaneous	4	Austria	Fossil	D	White, transparent and orange effl.	1	1		
MNHN.F.FO209	*Rosalina viennensis*	Hyaline	1	Hungary	Fossil	C	White effl.		1		
MNHN.F.FO222	*Alveolina pulchra*	Porcelaneous	1	Cuba	Recent	D	White and transparente effl.	1			1
MNHN.F.FO230.1	*Biloculina carinata*	Porcelaneous	2	Cuba	Recent	D	White and transparent effl.	2			
MNHN.F.FO257	*Nodosaria catesbyi*	Hyaline	5	Cuba	Recent	D	Transparent effl.		5		
MNHN.F.FO259	*Nodosaria punctata*	Hyaline	1	Cuba	Recent	D	Transparent effl.	1	1		
MNHN.F.FO262	*Nonionina sloani*	Hyaline	1	Cuba	Recent	D	White effl.	1	1		
MNHN.F.FO268	*Orbiculina compressa*	Hyaline	1	Cuba	Recent	D	White effl.	1			1
MNHN.F.FO273	*Puteolina proteus*	Porcelaneous	5	Cuba	Recent	C-D	White effl.-snowball	5			
MNHN.F.FO289	*Quinqueloculina dilatata*	Porcelaneous	1	Cuba	Recent	D	White effl.	1			
MNHN.F.FO296.1	*Quinqueloculina planciana*	Porcelaneous	1	Cuba	Recent	D	White effl.	1			1
MNHN.F.FO297.1	*Quinqueloculina sagra*	Porcelaneous	1	Cuba	Recent	D	White and transparent effl.	1	1		
MNHN.F.FO322.1	*Textularia candeiana*	Hyaline	1	Cuba	Recent	D	White effl.	1			1
MNHN.F.FO326	*Vertebralina cassis*	Porcelaneous	1	Cuba	Recent	D	White effl.	1			
MNHN.F.FO329.1	*Triloculina eburnea*	Hyaline	2	Cuba	Recent	D	White effl.-snowball	1			
MNHN.F.FO330	*Triolculina fichteliana*	Hyaline	3	Cuba	Recent	D	Transparent effl.	3			
MNHN.F.FO335	*Virgulina punctata*	Hyaline	1	Cuba	Recent	D	White effl.	1			1
MNHN.F.FO379	*Oolina compressa*	Hyaline	1	Cuba	Recent	D	Transparent effl.		1		
MNHN.F.FO398	*Quinqueloculina flexiosa*	Porcelaneous	2	Perou	Recent	D	White effl.-snowball	2			
MNHN.F.FO585	*Peneroplis planatus*	Porcelaneous	8	Australia	Recent	B-D	White and transparent effl.	5			"3 "
MNHN.F.FO626	*Rosalina squamosa*	Hyaline	8	n.a.	Recent	B-D	White effl.	8			
MNHN.F.FO734	*Bulimina obliqua*	Hyaline	8	France	Fossil	B-C	White and transparent effl.			7	
MNHN.F.FO774	*Faujasina carinata*	Hyaline	1	Holland	Fossil	D	White effl.	1			
MNHN.F.FO838	*Marginulina* sp.	Hyaline	1	n.a.	n.a.	C	White effl.			1	
Total			**66**					**42**	**12**	**8**	**8**

Terquem's mounting micro-environments: co-existing with acid releasing materials

The link between VOCs and wooden furniture was not established until the 30s (Nicholls 1934). Thus, when Terquem proceeded to the mountings of d'Orbigny's foraminifera, he could not know how critical it would be to introduce cellulose-based materials inside sealed tubes. For decades, the combination of cotton, blue paper and cork constituted a continuous source of VOCs. These compounds could not escape the tube and were thus reacting with the calcareous specimens to form calcium salts. This acidic atmosphere lasted in the tubes until the cork caps were removed.

Acid-sensitive *A-D strips* were used to estimate and compare the contribution of each material in these acidic emissions. Fig. 9 shows the colour change (ΔE) of the strips. It increases with the amount of acid emitted during exposure, thus highlighting the greater contribution of the blue paper in acidic emissions (ΔE = *c.* 23), followed by cotton (ΔE = *c.* 20) and, in a lesser amount, cork caps (ΔE = *c.* 14). White Whatman paper, made of cotton linters (100% cellulose, no additives) was also tested to compare with the historical blue paper, and appears far less pollutant (ΔE = *c.* 8). This result questions the potential role of the colouring agent (identi-



Samples	L*(D65)	a*(D65)	b*(D65)	ΔE*(D65)	RGB Color
Reference	47	–13	–22	–	
Whatman paper	49.3 ± 0.7	–15.6 ± 0.4	–14.3 ± 0.4	**8.5** ± 0.2	
Cork	51.2 ± 0.3	–16.8 ± 0.1	–9 ± 0.5	**14.2** ± 0.6	
Cotton	51.9 ± 0.9	–16.9 ± 0.3	–2.9 ± 0.9	**20.1** ± 0.8	
Blue paper	53.6 ± 0.2	–17.3 ± 0.1	0.2 ± 0.4	**23.5** ± 0.4	

Fig. 9. — Results of the colorimetric measurements made on A-D strips after exposure for 4 days to the storage materials. Acid sensitive A-D strips were exposed to 1g of each material, inside hermetic containers. When acids react with the A-D strips, the color change from blue to yellow so that the calculated change in colour (ΔE) can provide information on the relative amounts of acids emitted by the materials. The reference corresponds to the color of A-D strips before exposition. The results presented in the table indicate the blue paper is the most pollutant (highest ΔE), followed by cotton and cork. Figure by C. Hairie.

fied as Prussian blue) or additives in the ageing of the paper but would require deepest investigations (Kida *et al.* 2015). Taking into consideration the droplets observed inside some of d'Orbigny's tubes, it appears the foraminifera evolved in an acidic and humid micro-environment, that was enhanced by external environmental conditions discussed below.

The buildings of the Whale Courtyard: a first unhealthy place

The buildings of the Whale Courtyard were the first places to have stored d'Orbigny's collections after his death. Since they have been partly rebuilt and largely renovated, it is impossible today to assess precisely which type of environmental conditions they were imposing. Yet archival records attest that they were in a poor condition, humid and not good for health (Cardot 2012), which motivated the construction in the late 1890s of a new building on the west side of the garden to host all palaeontological collections.

Before Terquem's intervention in the 1870s, the specimens (mostly types) were placed between two glass plates without specific mounting. These basic mountings were piled-up in cardboard boxes, together with the sand bottles and the illustration plates. After Terquem's intervention, the collection has been probably stored in the wooden furniture that was claimed by Albert Gaudry, head of the palaeontology laboratory, for the protection of invertebrate fossil collections (Hairie *et al.* 2022). This furniture may have softened the impact of humidity on the palaeontological material in the premises that were not heated. Yet it would also have been a source of VOCs.

The new building on Buffon Street: still highly humid

The current palaeontology gallery, located on the Buffon Street, was built at the end of the XIXth century and inaugurated in 1898. We do not know with precision when the foraminifera collection moved there, but it was already installed in this building when the 1910 historic flood of the Seine took place (Table 4). The main testimony suggesting the foraminifera were flooded rests on Edward Heron-Allen's report, that was made four years after the disaster (Heron-Allen & Earland 1915; Hairie *et al.* 2022). Today, some of the labels on the sediment bottles seem to have been water-damaged (Chavanne *et al.* 2019), which suggests that the collection was indeed stored in the basement (Fig. 10A).

An undeniable consequence of the flood was the building insalubrity, as the basements remained humid for decades after the catastrophe. Between 1910 and 1912, the Professors' board kept discussing about unusual humidity conditions that compromised the conservation of palaeontological collections[2]. In 1937, Camille Arambourg, head of Palaeontology, was also complaining that the high level of moisture in the building was changing the physical properties of the glues used to stick the specimens that were coming off[3]. He also specified that the basements had been flooded several times[4], meaning that the 1910 flood of the Seine, although historically important, was not the only one that affected the laboratory. In fact, the building was situated at the intersection of two rivers, the Seine and the Bièvre, which contributed to the buildings recurrent humidity (Hairie *et al.* 2022).

D'Arambourg also complained about the poor condition of the palaeontology collections that were sometimes covered with mould (Hairie *et al.* 2022, appendix 8, part 1, pages 4-5). He furthermore mentioned the presence of cracks on the facades of the building, resulting in the penetration of moisture into the display cases and causing condensation at the surface of the fossils[3] (Hairie *et al.* 2022, appendix 8, part 2, pages 1-2).

Because WWII happened shortly after Arambourg's report, we can assume that these conditions did not change much in the following years, when the d'Orbigny collection moved with the invertebrate fossils to the second-floor gallery or in one of the d'Orbigny or Vibraye rooms. The humidity of the building and the high probability that the foraminifera collection was hidden in the basements during WWI and WWII, lead us to consider that the collection has been exposed to high moisture conditions for long periods. The sealing of the tubes with corks may have delayed water transfer inside the tubes but could not totally prevent it.

The palaeontology gallery: new premises with great variations of temperature

Arambourg's report not only pointed out humidity problems but also difficulties related to temperature fluctuations in the gallery where nothing was foreseen to insure the constancy of environmental parameters. According to him, these fluctuations were influencing considerably the conservation of the fossil bones assembled with glues of various natures, plaster, waxes or resins[3] (Hairie *et al.* 2022, appendix 8, part1, pages 4-5). The gallery was indeed designed according to Gaudry's wish of a large hall illuminated with day light (Fig. 10B). The double glass roof in the gallery and in the d'Orbigny room, combined with large windows in the *salle du Bassin de Paris,* should have provoked significant temperature variations by greenhouse effect in the whole building. The blackout blind system that was initially installed between the two glass roofs of the gallery is no longer in operation since, at least, the 1930s. An accurate assessment of past environmental conditions remains difficult, but we may reasonably suppose that the influence of the glass roofs on summer temperatures inside the building did not change much.

An illustration of these temperatures, recorded by the *Hanwell* live monitoring of the gallery in 2022 can be found on Fig. 11 (red curve). It shows a significant variation of the average temperatures from one season to another (over 35°C during August vs *c.* 20°C at the end of September) with diurnal fluctuations that can reach 5°C. As the showcases do not contain strong buffering systems, these changes of temperature lead to varying relative humidity conditions (Fig. 11, blue curve). Diurnal fluctuations of 7-8% RH are common and may sometimes reach 12% RH (Fig. 11 [14th August]). We also observe that the average humidity increase between August and September is more or less correlated to the decrease of temperature, which is expected. In addition, uncorrelated variations may happen, that can be explained by hygrometric conditions outside the building (weather change).

The combination of all these parameters results in large fluctuations of humidity in the gallery. For instance, an increase of 40% RH is observed between the 13th August and the 14th September 2022. Even if the current climate change emphasizes these effects, the environmental conditions of the foraminifera collection during the XXth century were obviously far from meeting the current conservation standards for fossil storage that recommend staying below 5% RH variation within a month (Johnson 1999).

The South Western side of the building: even worse conditions

The transfer of the collection operated in 1990 to the South Western side of the building (Table 4) did not really improve its environment: despite its more recent construction in the 1960s, the extension of the laboratory is also a thermal sieve, including several glass roofs. The two successive micropalaeontology reserves that housed the specimens between 1990 and 2019 have similar characteristics, with no windows and the use of metallic furniture. In 2014, following the repairs to the main staircase, isolation problems started to become unbearable for the staff and the collections. Walls were built next to the staircase in the lower levels to create storage spaces, which made things even worse: by limiting air exchanges, they emphasized the concentration of heat on the upper floors, already important because of the glass roof. Since then, summer temperatures below the glass roof in the researchers' offices could culminate at 45-50°C. Finally, in 2019, it was decided to transfer the collections into a new air-conditioned storage building situated on the opposite side of the Buffon Street (Table 4).

A new storage building: air conditioned but imperfect control of humidity

The problems encountered by the d'Orbigny collection are probably not entirely solved. The new storage building gathers in one place all the MNHN micropalaeontology collections, thus facilitating their management. Yet, the air-conditioning system does not provide optimal conditions. It is relatively effective to limit the variations of temperature but not well designed in the management of humidity, especially when the air that comes from outside has to be dried. Recent hygrometry surveys have shown that humidity is not stable, with values exceeding 70% HR for several days. This situation is particularly delicate in summer, when outside weather is unusually warm and humid (because of current climatic change). A way to limit this issue consists in allowing an increase of temperature inside the building, but this is not always enough.

DISCUSSION

Calcium formates, but no detection of calcium acetate

The non-detection of calcium acetate on the foraminifera is unusual in the context of Byne's decay as calcium acetates are known as its main degradation by-products (Eggert *et al.* 2021). Indeed, acetic acid concentrations measured

FIG. 10. — Sediment bottles collected by d'Orbigny exhibited in the Salle du Bassin de Paris (**A**) and overview of the palaeontology gallery (**B**). The traces of water damage noticed on the labels of the sediment bottles could find their origin in the Seine flood of 1910 (**A**). View of the Palaeontology main gallery from the balcony, next to the *Salle du Bassin de Paris*, showing a double glass roof (**B**) that brings natural light but is also responsible of greenhouse effect. The presence of numerous glass roofs, combined with the poor isolation of the building results in high temperature fluctuations. Similar observations can be formulated for the 1950s extension where the micropalaeontology reserve was located between the 1990s and 2019 (see Table 4). Photos: C. Hairie.

in museum displays are usually higher than those of formic acid concentrations (Gibson & Watt 2010). This induces a major occurrence of acetate-based compounds, merely anthropic, such as calcium acetate mono- and hemi-hydrate [$Ca(CH_3COO)_2{\cdot}H_2O$ & $Ca(CH_3COO)_2{\cdot}1/2H_2O$] (Tennent & Baird 1985), mixed formate-acetate salts (such as $Ca(HCOO)(CH_3COO){\cdot}H_2O$), calclacite [$Ca(CH_3COO)Cl{\cdot}5H_2O$] or thecotrichite [$Ca_3(CH_3COO)_3Cl(NO_3)_2{\cdot}7H_2O$] (Eggert *et al.* 2021). Unfortunately, in the present study, qualitative or quantitative analysis of the pollutants present in d'Orbigny's glass tubes was impossible: the atmosphere under which the foraminifera have evolved is no longer accessible since the recent removal of all the cork caps to protect the specimens from the acids (see part "Considered specimens and pictures"). Yet, given the cellulose-based nature of the polluting materials, it is reasonable to assume that acetic acid and formic acid emissions inside the tubes were of the same order.

The omnipresence of pure calcium formate salts in the collection is confusing as it is almost impossible, in laboratory conditions, to obtain these salts from saturated solutions combining formate, acetate and calcium. Indeed, these types of solutions mostly lead to the formation of mixed formate-acetate salts such as $Ca(HCOO)(CH_3COO){\cdot}H_2O$ (Bette *et al.* 2019).

Moreover, there are almost no mentions in the literature of calcium formate salts as Byne's degradation by-products. The orthorhombic phase [α-$Ca(HCOO)_2$] was only detected on calcareous objects placed in contact with glass or polluted surface after disinfection with aqueous formaldehyde (Komarèk 1957), and, very recently, on pearls of the Hildesheim Bernward Cross (Eggert & Fischer 2021). These occurrences do not mention the tetragonal calcium formate [ß-$Ca(HCOO)_2$] and remain limited in comparison to those dealing with calcium acetates (Eggert *et al.* 2021).

What we know about calcium formates is rather paradoxical. The α-$Ca(HCOO)_2$ polymorph is known as the stable thermodynamic phase because it forms easily in a saturated solution and is stable at ambient conditions (Chukanov *et al.* 2021). Yet it seems to exist -almost- only in laboratory conditions, whereas the ß-$Ca(HCOO)_2$ can be found in nature under the rare mineral form named *formicaite,* discovered in Russian mines (Chukanov *et al.* 1999, 2021; Warin 2022). In spite of that, ß-$Ca(HCOO)_2$ was proved to be unstable (or metastable) when synthetized in laboratory (Schutte & Buijs 1964). It can be obtained by adding solvents in an aqueous solution of calcium formate or by heating the α-polymorph after crystallization at 300°C (Mentzen 1971). But at ambient temperature and humidity conditions (25°C, 50% RH), it is rapidly converted into the α-polymorph (Schutte & Buijs

1964). The only way to make the ß-$Ca(HCOO)_2$ polymorph stable is to keep it under dry environments (0% RH). This behaviour remains unexplained since (i) the two polymorphs are anhydrous and (ii) the humidity is much higher than 0% RH around formicaite deposits or inside the MNHN facilities. Current investigations aim at understanding the formation and stability of ß-$Ca(HCOO)_2$ on the d'Orbigny foraminifera collection (Hairie *et al.* in progress).

Sodium formate, but no sodium acetates

Similarly, the analyses that were performed on the glass inside the tubes did not point out sodium acetate but sodium formate (see part: "Characterization of the "droplets" inside the glass tubes"). This phase corresponds to a common degradation product often observed on soda-glass exposed to VOCs emission (Robinet *et al.* 2004). When water condenses, it may diffuse in the sub-surface of the glass, hydrate available ions and form a gel-layer at the surface of the glass. In polluted environments, organic acid vapours such as formic or acetic acids can react with this gel, leading to the precipitation of organic salts under low RH conditions (Tennent & Romich 1999).

The non-detection of sodium acetate does not necessarily mean that there is no surrounding acetic acid. It should be pointed out that sodium acetate is a highly hygroscopic phase that deliquesces at low relative humidity (RHeq~ 43–45%; Peng & Chan 2001). Sodium formate is also hygroscopic but deliquesces at higher relative humidity (RHeq~ 50-60%; Beyer & Steiger 2010; Gibson & Watt 2010). Keeping in mind that the deliquescence point of a salt might be lowered by the presence of another one, it seems very plausible that sodium acetate remains dissolved in the porous structure of the glass while sodium formate precipitates when relative humidity is sufficiently low.

Similar considerations cannot be put forward to explain the non-detection of calcium acetate. Indeed, calcium acetate has a much higher deliquescence point than sodium acetate (RHeq = *c.* 91.5% ± 1%; Guo *et al.* 2019). Even if the presence of other salts (such as magnesium acetate or sodium acetate) may lower its deliquescence point, calcium acetate, if present, should be crystalized at room temperature (50-55% RH).

It is reasonable to suppose that calcium acetate has gone unnoticed by Raman spectroscopy during the foraminifera analyses because its signal was hidden by fluorescence phenomena, meaning that other analysing tools should be foreseen. Micro XRD measurements may help get a clearer insight on calcium acetate salts formation, as XRD remains the best technique to characterize Byne's salts. However, since the specimens cannot be removed from their glass slides, they must be performed *in situ* if possible on a well-equipped synchrotron beamline, which could not be undertaken in the present study.

Impact of the intrinsic characteristics of the foraminifers

Porcelaneous vs hyaline foraminifera

This study shows that the hyaline/porcelaneous nature of foraminifera influences the degradation: hyaline foraminifers are less prone to degradation than porcelaneous ones. Their behaviour during degradation also seems different: dissolution, which can be considered as an early stage of the degradation, is mostly observed on hyaline specimens, while crystalline growth is more noticeable on porcelaneous ones.

These results are in line with oceanographic observations that established a higher fragility of porcelaneous foraminifera (Miliolida) in the context of acidified sea water (Milliman 1975; Smith & Nelson 2003). This higher sensitivity could be explained by the fact that porcelaneous foraminifera contain higher amounts of magnesium and smaller crystals of calcite (de Nooijer *et al.* 2023). Indeed, during biomineralization of porcelaneous tests, magnesium competes calcium in the formation of carbonates, which makes calcite less crystalline. It is thus more prone to dissolution phenomena in marine environments, when there is a decrease of pH because of CO_2 levels or during diagenetic processes.

In our study, magnesium formate was also observed among degradation products, yet both on porcelaneous and hyaline specimens. This point is rather unusual since magnesium formate is rarely mentioned in the literature: it was only observed on ceramics (Eggert *et al.* 2019) and on a dolomitic [$CaMg(CO_3)_2$] sandstone that was submitted to a 'cleaning' treatment using formic acid (Zehnder & Arnold 1984). The statistic of our analyses (66 foraminifera) is too low to highlight a correlation between the occurrence of magnesium formate and the porcelaneous/hyaline nature of the foraminifer, especially if considering the variability in Mg/Ca geochemistry within hyaline foraminifera. Recent results indeed show that Rotaliida can have more or less magnesium in their test, so that this order does not always reflect "the low magnesium content" of hyaline species as expected (de Nooijer *et al.* 2023). However, despite this variability, the rotaliid foraminifera have on average a lower magnesium content than the Miliolida. Future analyses should take these chemical variabilities into consideration to refine the results.

Still, a high magnesium content in the foraminifera tests may play a role in the crystallisation of degradation by-products: within our Raman analyses (Table 3), formation of magnesium formate di-hydrate was observed on 8 foraminifera (upon 66). It was always associated with β-calcium formate but not with a-calcium formate. Moreover, magnesium formate di-hydrate and β-calcium formate grow under relatively similar white dendritic crystals. This raises questions about the possible impact of magnesium ions toward the stabilization of the metastable β-calcium formate.

Recent vs fossil foraminifera

This study shows that once the decay is launched, the rate of damage is influenced by the age of the specimen (recent vs fossil as depicted in part "Influence of the nature and age of the foraminifera tests"). Table 2A indeed shows that recent specimens sampled at sea appear more fragile compared to fossil ones: statistically, they are two times more susceptible to develop intense damage (grad D-E). A similar behaviour was also observed in a previous study on seashells undergoing Byne's decay (Tennent & Baird 1985).

TABLE 4. — The different locations of the d'Orbigny foraminifera collection, Paris, from the XIXth century to nowadays and their corresponding environmental conditions. These data, collected and interpreted from archival records, are described elsewhere in full details (Hairie *et al.* 2022). They helped to estimate temperature variations that could occur from one location to another. The number of + indicates the amplitude of these temperature variations.

		The Jardin des Plantes, Paris								
			The Palaeontology building on the Buffon street							
			North Eastern side					South Western side		
	The family house, Pierrefitte sur Seine	**The buildings of the Whale courtyard**	**Basements**	**Palaeontology laboratory 1st floor**	**D'Orbigny room, 2nd floor**	**Vibraye room, 2nd floor**	**The Galleries**	**4th floor, storage room near offices**	**3rd floor, dark room**	**New storage opposite side of the Buffon street**
From July 1853 to end 1853	Sediment bottles and specimens									
From 1854 to Jan. 1858	Sediment bottles and specimens									
From Jan. 1858 to the end of the XIXth c.		Sediment bottles & mounted specimens								
From begining of XXth c. to Jan. 1910			Sediment bottles and probably mounted specimens	Maybe mounted specimens						
From Jan. 1910 to the 1930s			Probably during the two World Wars for protection against bombings	Most of the collection			maybe part of the collection			
From the 1930s to the 1960/70s					Sediment bottles and mounted specimens					
From the 1960/70s to 1990				Mounted specimens	Sediment bottles					
1990-2014					Sediment bottles			Mounted specimens		
2014-2019							a few sediment bottles and mounted specimens		Mounted specimens	
2019-today										Sediment bottles and mounted specimens
Environmental conditions	?	The building is humid not to say unhealthy. Half of the building has been destroyed	High humidity conditions, slow and limited variations of temperature (excepted for the area next to the boiler room)	Small storage room with no windows and poor isolation	Double glass ceiling but no window	Large windows on the North Eastern side – Direct opening on the gallery	Numerous windows and a double glass ceiling provoke large diurnal variations of temperature	Last floor. Small storage room than opens on an office with large windows	The dark room opens on a stair well equipped with a glass roof	Air conditionning system by insufficient in the monitoring of humidity
Temperature var.	?	?	+	++	+++		++++	+++	++++	no

Three hypotheses may explain this observation. The first deals with diagenetic processes that would "stabilize" the test by increasing calcium carbonate crystallinity. *Recent* specimens went through no to only weak levels of diagenesis. In contrast, fossil foraminifera have undergone some degree of diagenetic processes such as dissolution and recrystallisation during sediment burial. As a result, the size of the $CaCO_3$ crystals in the fossil tests would tend to be coarser (larger) than the non-diagenised tests of recent foraminifera (Sexton *et al.* 2006; Sexton & Wilson 2009). In this respect, the recent foraminifera, collected in marine environments, would be more susceptible to acidic VOC attack due to their lower crystallinity.

A second hypothesis involves the presence of chemical species such as seawater-soluble salts that may promote the decay. Indeed, water salinity approaches 35 g/L for oceans, and mostly corresponds to sodium chloride, magnesium chlorides and sulphate salts (Millero *et al.* 2008). Some of these salts being highly hygroscopic, they could maintain a humid atmosphere around the specimens (Díaz Gonçalves *et al.* 2006). This would favour condensation within the specimen and dissolution of calcium carbonate by acidic vapours. Yet, none of these salts was pointed out during our analyses, meaning that additional work should be done to evidence their presence and study their impact.

A third hypothesis lies in a plausible impact of organic residues that would remain in the test and favour the degradation: these residues may still be present in recent/sub-recent foraminifera, whereas they would have disappeared during diagenesis of the fossil tests, This hypothesis however needs further investigations, as the role of organic matter in *Byne's decay* remains unknown.

Unsuitable preparation or inadequate housing material?

The development of organic salts on heritage collections is usually attributed to the use of inappropriate storage materials that emit VOCs. In the case of palaeontology specimens, the frequent use of acidic chemicals to extract fossils from sediments represents an additional source of contamination that is most of the time not evaluated and cannot always be neglected (Bourdon 1957, 1962; Lindsay 1986). Yet, we know that d'Orbigny was collecting foraminifera from soft sediments and isolated them from water-washed sands, meaning that the use of acids was not necessary, and thus unlikely. Regarding the d'Orbigny's collection, the scenario of contamination with an acidic extraction of the foraminifera can reasonably be ruled out.

The reason of d'Orbigny's collection being threatened by calcium salts mostly lies on the use of VOCs-releasing materials for the mounting of the foraminifera. Whether it is in Paris or La Rochelle, the presence of cellulosic material such as cork, cotton or paper implies significant VOC's emissions (Shahani & Harrison 2002; Gibson & Watt 2010). Yet, the results of the *A-D strips* test incriminate the blue paper and cotton as the most polluting materials. Given that these materials are absent from the La Rochelle tubes, it seems less surprising to observe little or no degradation on them. The presence of cork and white paper may have been responsible for the degradation of the glass but was certainly not enough to attack the specimens of La Rochelle.

The use of adhesives to fix or varnish palaeontology specimens may represent another potential source of acids that also deserves discussion. Indeed, in the middle XXth century, Pierre Marie[5], a micropalaeontologist who worked on the d'Orbigny collection, pointed out acidic emissions that he was attributing, whether rightly or wrongly, to the decay of adhesives (Hairie *et al.* 2022). In one of his correspondences, he discussed the fragility of microscopic collections. According to him, the putrefaction of the glue, when exposed to humid conditions, results in the emission of acids that attack the specimens' shells and make them fall into dust. He unfortunately did not specify which type of adhesive he was using but interestingly mentions that some of his own collections was lost in less than three years, which represents a short time in comparison to d'Orbigny's collection and thus a high speed of degradation. This account also recalls the case of the Basset's mountings at La Rochelle, in which specimens are embedded in gelatine glue. It remains difficult to assess if their poor state of conservation (their surface texture seems lost) is due to the adhesive or if the adhesive was applied to "stabilize" them because they were already highly fragile.

In the case of the Paris collection, we should acknowledge that the mountings on the glass slides were carefully made, and no embedding of the foraminifera are observed. At best we suspect that some of the breaks noticed on mechanically damaged foraminifera (Ex. Fig. 4, specimen B5) were due to a withdrawal of adhesive provoked by relative humidity variations, especially where dry conditions are achieved. Therefore, the pollution from which the specimens have suffered seems directly related to the materials placed inside the tubes (cork, blue paper and cotton), and, to a lesser extent (because the tubes were sealed) to the oak furniture in which the collection was stored.

The impact of fluctuating temperature

Since its acquisition in 1858, the d'Orbigny collection of the MNHN, Paris, was moved in several places where humidity and temperature were not monitored (Table 3). The Paris Palaeontology building was humid and poorly isolated. It was also equipped with glass roofs that imposed, in summer, high temperature conditions (see part "The palaeontology gallery: new premises with great variations of temperature"). At La Rochelle, the d'Orbigny collection was stored in the attics of a single building, also with unstable temperature conditions but probably less humid (no flooding) and less warm in summer. As a result of these two different climates, the specimens in tubes that have been sealed with corks in both collections, behaved very differently. The Paris foraminifera are deeply impacted by Byne's decay, while the foraminifera from La Rochelle seem spared. Similar consideration can be formulated for the glass of the tubes: condensation droplets of saturated magnesium formate solutions are observed inside the glass tubes housed in Paris while only tiny traces of alteration are visible on those of La Rochelle.

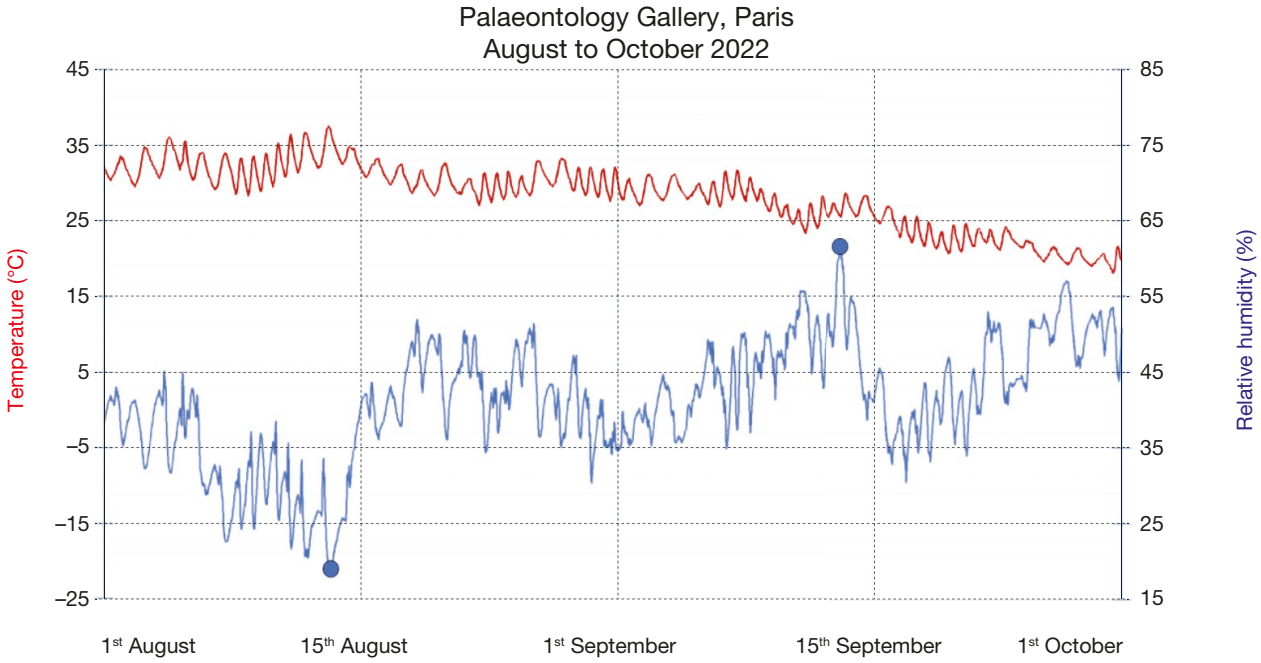


FIG. 11. — Environmental data collected in the Palaeontology gallery between August 2022 and October 2022 (from Hanwell device n°208). Numerous variations of relative humidity (**RH**, in **blue**) are uncorrelated with temperature variations (in **red**), which proves the poor isolation of the building and contribution of outdoor humidity. The important heatwave of mid-August corresponds to the lowest RH value, while, on the opposite, the highest values matches with humid weather. RH variations in the gallery lies between 10-30%. Temperature values during the period are also much higher than recommendations for museums (*c.* 20°C), with several peaks over 35°C in summer.

Several points explain these different behaviours. Firstly, the temperature. It controls VOC's production and diffusion coefficients: it has been proven that release of acetic acid increases by factors of 7-11 when the storage temperature of a wood material increases from 20 to 45°C (Gibson & Watt 2010; Wang *et al.* 2021). Similar behaviours can be expected for the cellulose-based materials that were present inside the tubes, such as cork, paper and cotton. Moreover, high temperature conditions favour evaporation and thus crystallization of degradation products. The Paris collection having experienced higher temperatures than the one housed at La Rochelle, is thus more severely damaged.

Secondly, the relative humidity. At 25°C, sodium formate deliquesces at approximatively 55% RH (Peng & Chan 2001). The observation of liquid droplets within the Paris glass tubes in july, when temperature was over 25°C, indicates that relative humidity inside these tubes was over 55-60%. Considering that the previous sealants were hermetic enough, absolute humidity inside the tubes would have remained unchanged all along the year. According to the psychrometric diagram, which presents the physical and thermal properties of moist air, the relative humidity could then easily reach 100% when temperatures went down to 18-20°C. These considerations suggest that: 1) the foraminifera have experienced high fluctuations of RH inside the tubes because of temperature variations outside the tubes (diurnal or seasonal); and 2) this humidity is specific to the Paris collection because the collection was stored in a humid building, not only because of the 1910 flood, but also because of a poor isolation and the Bièvre and Seine rivers proximity.

This comparison between the collections of Paris and La Rochelle helps us to put forward that storage materials were not sufficient to provoke the degradation. This latter is also largely promoted by fluctuations of temperature that induced high variations of relative humidity inside the tubes, and cyclic alternance of condensation/dissolution and evaporation/precipitation reactions.

CONCLUSION

The d'Orbigny foraminifera collection, one of the most valuable micropalaeontology collections housed at the National Museum of Natural History, Paris, is experiencing Byne's decay. To get a deeper insight of the damage extent, a conservation report was undertaken. It allowed to trace the material history of the collection and to describe with more precision the alterations observed on the specimens.

The material history and condition of this collection were retraced through archival records, such as the Lys' files, and compared with a much better-preserved foraminifera collection, also collected by d'Orbigny's but housed at La Rochelle since then. This approach led to the conclusion that the degradation of the Paris collection occurred progressively and had probably already started at the beginning of the XXth century, or even earlier. Indeed, the introduction of polluting mounting materials and the confinement of the foraminifera in sealed tubes during the 1880s appear as the origin of the degradation. Climate variations did the rest. Several floods,

including the spectacular 1910 Seine flood, have certainly brought a lot of moisture in the building, but they cannot be considered as the only cause of all the damage observed on the collection. The glass roofs of the "new" building inaugurated in 1898 certainly contributed in a more extended way to the decay. By greenhouse effect, they provoked high fluctuations of temperature in the building, which also induced great variations of humidity conditions inside the sealed tubes. On one hand, high temperatures were promoting emissions of VOCs and inducing low relative humidity conditions inside the tubes, thus favouring crystallization. On the other hand, low temperature values were inducing high relative humidity conditions inside the tubes, thus favouring micro-condensation of water in the foraminifera porosity and dissolution of already emitted VOCs.

Byne's decay usually corresponds to the growth of crystalline organic salts on calcareous specimens or objects. Our study pointed out other features, not reported in the literature, that seem specific to the microscopic size of the specimens. They deal with dissolution phenomena smoothening the surface texture of the test that becomes more transparent. Although less spectacular, these alterations jeopardize the legibility of the specimens and seriously limit their use for scientific purpose.

Among the 3621 specimens of the Paris collection, 444 are entirely ruined (Grade D+E) and 582 are hardly recognisable (Grade C), meaning that 28% of the collection is lost for research. The remaining 72% of the collection that can still be used for scientific purpose is divided between the foraminifera in excellent conditions (Grade A, 39%) and those that are slightly damaged but still recognisable (Grade B, 33%). *Cracks* purely provoked by mechanical stress are also noticed. Yet 45% at least of the collection is damaged by more or less advanced Byne's decay. Taking into consideration all possible features related to this degradation, such as dissolution phenomena, this proportion raises up to 59%.

The present study shows that the hyaline or porcelaneous nature of the test also has an impact on its degradation. *Hyaline* species are more prone to dissolution phenomena while porcelaneous species (which test is composed by calcite crystals with higher amount of magnesium) are more affected by organic crystalline growths. The age of the foraminifera also has some influence, recent specimens sampled at sea coastal-offshore environments being more prone to Byne's decay than fossil ones coming from continental outcrops.

Identification of crystalline growths by Raman spectroscopy was achieved and highlighted unexpected crystalline phases. It was first noticed that VOCs were not only affecting the specimens but also the glass of the tubes on which sodium formate was identified. Growths of calcium and magnesium formates were pointed out on the specimens, the ß-polymorph of calcium formate being largely predominant. This observation was particularly puzzling since ß-calcium formate is known to be unstable at room temperature in presence of some humidity in the air. Some calcium lactates, which origin remains unclear, were also identified. Even more astonishing was the non-detection of calcium acetates that are the most common Byne's degradation by-products. This non-detection may be due to some bias of the technique. Since the salts were often fluorescent, Raman analyses were sometimes limited, meaning that calcium acetate may have gone unnoticed. In the near future, other tools such as X-ray microdiffraction should also be foreseen to confirm the absence of calcium acetates.

Pure calcium formates are rarely mentioned as Byne's degradation by-products on heritage objects. Their presence, combined with the non-detection of calcium acetate or mixed formate-acetate salts, raises questions about the chemistry happening at the microscopic scale that should be addressed by future artificial ageing of foraminifera in presence of different combinations of VOCs. In waiting of these results, it is important that the foraminifera remain stored in aerated mountings, with limited variations of temperature or humidity.

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Statements and declarations, authors interests
The authors declare that they have no competing interest.

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APPENDIX: END NOTES

[1] Private communication with Elise Patole-Edoumba, Director of the Museum of natural History, La Rochelle. No temperature or humidity records of the former reserves are available.

[2] « *Monsieur Boule fait signaler l'état d'humidité de la galerie de Paléontologie, où de nombreux objets se décollent.* » – Assemblée des professeurs. Séance du 15 décembre 1910.

[3] Arambourg's report, part 2, page 1-2 : « […] *Le tassement de la partie Est du bâtiment et les lézardes qui en résultent sur les façades Nord et Sud sont bien connues* […] *je signale : 1) que les deux lézardes en question mettent en communication avec l'extérieur, par une fissure qui atteint plusieurs centimètres de large, l'intérieur des vitrines latérales. Il en résulte a) une pénétration d'humidité, qui recouvre parfois l'intérieur des vitrines d'une couche de buée, et provoque la condensation d'eau à la surface des* fossile*s* […] ».
Arambourg's report, part 1, page 4-5 « […] *De plus, les variations considérables de température et d'état hygrométrique de la galerie où rien n'a été prévu pour assurer (comme dans les Musées modernes) la constance de ces états, influent considérablement sur la conservation des ossements* fossile*s dont les fragments sont assemblés avec des colles de natures diverses, du plâtre, des cires ou des résines, matériaux hétérogènes dont le mélange ne résiste pas aux intempéries* […] ».

[4] Arambourg's report, part 1, page 5: « *Les sous-sols des bâtiments de la Place Valhubert contiennent aussi des collections importantes* […] *du fait de l'humidité des sous-sols et des inondations qui ont eu lieu à plusieurs reprises, faute d'entretien, la poussière et les insectes rongeurs d'étiquettes y exercent des déprédations plus graves encore que pour les autres séries.* »

[5] Pierre Marie, correspondence with Dr Henri Allix, 1947 – consulted the 15th april 2022, CR2P archives, MNHN, Paris « […] *Cette détérioration, qui provoque souvent la ruine totale des collections de petits organismes, tient au fait que des traces d'humidité font travailler la colle, qui retient les spécimens. Elle se putréfie et libère des acides qui attaquent les coquilles – au moindre choc, ces dernières tombent en poussière et sont inutilisables* […] *J'ai appris ces inconvénients à mes dépends, mes premiers matériaux d'études, pour lesquels j'avais apporté tous mes soins en orientant mes plus beaux spécimens sont devenus inutilisables au bout de 3 ans* […] ».