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▶ To cite this version:

Clara Hairie, Marie Béatrice Forel, Annachiara Bartolini, Véronique Rouchon. The foraminifer and ostracod collections of the Muséum national d'Histoire naturelle, Paris: a key but fragile scientific heritage in a context of global warming. Heritage for the future, Science for Heritage, A European Adventure for Research and Innovation, Mar 2022, PARIS, France. hal-03826957

HAL Id: hal-03826957

https://hal.science/hal-03826957

Submitted on 24 Oct 2022

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Cultural heritage facing climate and environmental change

The foraminifer and ostracod collections of the Muséum national d'Histoire naturelle, Paris : a key but fragile scientific heritage in a context of global warming

Clara HAIRIE¹, Marie Béatrice FOREL², Annachiara BARTOLINI³, Véronique ROUCHON⁴

¹PhD Student, Centre de Recherche sur la Conservation (UAR3224) CNRS-MNHN-MC, France

² Associate Pr MNHN, Centre de Recherche en Paléontologie-Paris (UMR7207) CNRS-MNHN-SU,

³ Pr MNHN, Centre de Recherche en Paléontologie-Paris (UMR7207) CNRS-MNHN-SU, France

⁴ Pr MNHN, Centre de Recherche sur la Conservation (UAR-3224) CNRS-MNHN-MC, France

Keywords: Byne, fossils, efflorescence, organic salts

Abstract : The Muséum national d'Histoire naturelle houses collections of foraminifers and ostracods that are endangered by indoor pollutants. Alteration by-products consist in calcium organic salts, most of them including acetates in their composition. Unexpectedly, analyses of damaged specimens pointed out calcium formates as major degradation products, despite the presence of acetic acid in the environment. These observations highlight the need of a better understanding of the mineralogy and behaviour of calcium organic salts at varying temperature and humidity conditions.



Particularly abundant in aquatic and mostly marine ecosystems, foraminifers and ostracods provide valuable information on the environmental parameters that are conducive to their growth, such as water temperature or salinity. These micro-organisms, whether fossil or current, are considered as effective biomarkers. Fossil specimens are widely used for the reconstruction of paleoenvironments. Current specimens, collected several decades ago, can also be compared with newly collected material to measure the environmental impact of anthropogenic pressure and climate change (temperature rise, decrease in salinity due to ice melting, pollution, etc.).

Different types of collections

The Muséum national d'Histoire naturelle (MNHN), Paris, houses large collections of foraminifers and ostracods, the most prestigious of which being the d'Orbigny's collection acquired in 1858. Alcide Dessaline d'Orbigny was a pioneer in the field of palaeontology and biostratigraphy. Originating from La Rochelle, he dedicated his life to the study of foraminifers of which he published the first classification in 1826. A chair of Palaeontology was specifically created for him in 1853 at the MNHN but he died shortly after, in 1857. His succession at the MNHN was chaotic and his foraminifer collection was somehow neglected. After the 1870's war, research in micropalaeontology at the MNHN was mainly carried by two geologist enthusiasts, Olry Terquem (1797-1887) and Charles Schlumberger (1825-1905) who sorted, filed and remounted the d'Orbigny collection. Some of their personal material also joined the MNHN collection. After the Second World War, the development of oceanography and stratigraphy led new interests in foraminiferal studies, which also participated to the increase of the collections.

Different types of damage

Many of these collections suffer from Byne decay (Figure), a phenomenon that takes its name from Lotfus St George Byne who first described this type of alteration observed on shell specimens stored in oak cabinets¹. This alteration is related to indoor pollutants. Indeed, the tests, made of calcareous materials, are sensitive to Volatile Organic Compounds (VOCs) emitted by storage materials² such as paper, wood, adhesives, paints, rubbers, etc. The interaction of acidic VOCs with the calcareous matrix leads to formation of calcium salt efflorescence. As alteration products generally include some acetate in their formula, acetic acid is often pointed out as the main cause of degradation.



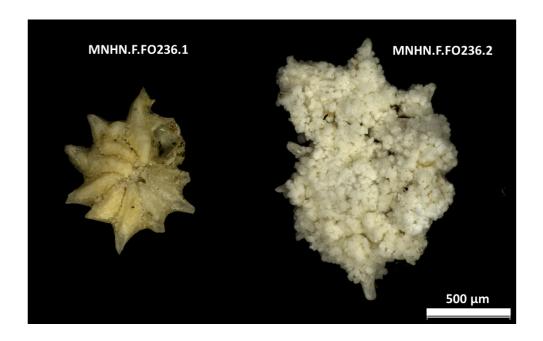


Figure : Two specimens of the foraminifer *Calcarina calcar* belonging to the d'Orbigny's collection. On the left, the specimen is in a fair condition. On the right, the specimen is severely damaged by calcium formate crystalline growth ©MNHN

Damaged specimens from different micropalaeontological collections were selected for analyses by Raman microspectroscopy (InVia, Renishaw, 732 nm laser, x50 objective, 10 acquisitions for 1 second). This technique was chosen because it can be performed in situ in a non-destructive way on small crystals of a few microns.

Surprisingly, calcium acetate hemi hydrate [Ca(CH₃CO₂)₂ $0.5H_2O$] and mono hydrate [Ca(CH₃CO₂)₂ H_2O] were not detected. Calcium formate acetate monohydrate [Ca(CH₃CO₂)(HCO₂) H_2O] was detected but in minor amounts, the main degradation phase corresponding to the tetragonal form of calcium formate [β -Ca(HCO₂)₂]. This point is all the more tricky as this phase is known to be unstable in environmental condition³. This polymorph of calcium formate was also exclusively found on a collection dating from the 1970's, and stored in a laboratory where fossils were periodically extracted by the use of concentrated acetic acid. Despite the use of fume hoods, one could easily and periodically smell the odour of acetic acid in this environment. Yet the collections seem in fair condition. A few ostracods only were altered and the damage concerned exclusively formation of calcium formate.



These observations illustrate the variety of degradation by-products occurring during Byne decay and clearly question the mechanism of their formation. Moreover, many of these salts are scarce and do not exist in the nature. Their occurrence is due to anthropogenic activity and their physico-chemical properties remain to be explored. Indeed, the behaviour of these salts in varying conditions of temperature and humidity is a key parameter of degradation mechanisms. In order to save energy and money, it is tempting to make more flexible the temperature and humidity conditions of storage rooms. Yet variations of these parameters may have some consequence on degradation mechanisms involving salt formation. Anticipating this impact necessitates a better knowledge of the hygroscopic properties of these salts and a better understanding of alteration mechanisms underlying these crystal growths.

Acknowledgment

This work is supported by the Fondation des Sciences du Patrimoine - Ecole universitaire de Recherche Paris Seine Humanité, Création, Patrimoine, Investissement d'avenir ANR-17-EURE-0021.

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This article is published within the framework of the European symposium "Heritage for the Future, Science for Heritage: A European Adventure for Research and Innovation" which will be held on 15 and 16 March 2022 at the Musée du Louvre and the National Library of France (François Mitterrand). This symposium is organized with the support of the European Commission and in partnership with the French Ministry of Culture, the French National Centre for Scientific Research (CNRS) and the universities of Paris-Saclay and Cergy Paris. To feed the symposium programme, a Call for Papers was launched in June 2021 and addressed to researchers, doctoral students, and various actors who contribute to the production, valorisation, dissemination and applications of knowledge such as heritage professionals, political decision-makers, international organisations etc. As a result of this Call for Papers, some proposed communications have been selected for publication on the symposium website in the form of short articles.