

Available online at www.sciencedirect.com

SciVerse ScienceDirect

www.elsevier.com/locate/matchar

Origin of growth defects in pearl

Xavier Bourrat^{a,b,c,*}, Li Qiao^d, QingLing Feng^d, Martine Angellier^{a,b,c},
Aurore Dissaux^{a,b,c}, Jean-Michel Beny^{a,b,c}, Vincent Barbin^e, Philippe Stempflé^f,
Marthe Rousseau^g, Evelyne Lopez^h

^aUniversité d'Orléans, ISTO, UMR 7327, 45071 Orléans, France

^bCNRS/INSU, ISTO, UMR 7327, 45071 Orléans, France

^cBRGM, ISTO, UMR 7327, BP 36009, 45060 Orléans, France

^dTsinghua University, Department of Materials Science and Engineering, Beijing 100084, China

^eReims Champagne-Ardenne University, GEGENAA, 2, Esplanade Roland-Garros, 51100 Reims, France

^fInstitute FEMTO-ST, ENSMM, 26 Chemin de l'Épitaphe, F-25030 Besançon Cedex, France

^gNancy University, Physiopathology and Articular Pharmacology, 9 Avenue de la forêt de Haye, BP 184, 54505 Vandœuvre les Nancy, France

^hMuseum National d'Histoire Naturelle USM 401-CNRS UMR7108, 43 rue Cuvier, 75231 cedex05 Paris, France

ARTICLE DATA

Article history:

Received 3 November 2011

Received in revised form 10 July 2012

Accepted 12 July 2012

Keywords:

Biomineralisation

Vaterite

Aragonite

Cathodoluminescence

Rock Eval

HPLC

FTIR

ABSTRACT

Pearls are produced from a natural biomineralisation process. The structural unit is a biocrystal whose formation is controlled by organic molecules. In the present paper we studied a major growth defect to highlight the role of the organics in the growth mechanism. Some freshwater pearls exhibit a lack of lustre, also known as 'milky pearl' defect. This defect is related to the formation of vaterite instead of aragonite during the biomineralisation growth process. We used Rock Eval pyrolysis, a new technique in this field, to quantify a noticeable increase of the organic matrix in milky pearls. At least 20% more organics were found when vaterite forms than aragonite. To further study its role during the growth process, the organic matrix was extracted using three different protocols and characterised by infrared spectroscopy (FTIR) and liquid chromatography (HPLC). The fraction of the organic matrix which is soluble in water (WSM fraction) was significantly different when analysed by FTIR and by HPLC. This fraction is very likely occluded within the mineral (intracrystalline matrix). To examine its role, WSM extracted from milky pearls was used as additive in controlled calcium carbonate growth experiments. In this case, vaterite crystals were obtained for the greater part. When WSM extracted from healthy pearls was used, aragonite and calcite crystals were grown. The polymorph (vaterite vs aragonite) appeared to be clearly connected to the WSM organic fraction. Several hypotheses may explain this result: *e.g.*, a minor disorder of the organic composition of the extrapallial fluid, an excess of Mn or Mg or a blocking of the growth at a transient stage. Finally, we propose to use cathodoluminescence as a non-destructive technique to sort these defective pearls.

© 2012 Published by Elsevier Inc.

1. Introduction

Nacre, or mother of pearl, is a mineralised tissue that is produced to toughen the mollusc shell and increase its

mechanical performance. Toughening is achieved by following the strategy of a dynamic multi-scale hybrid [1], where the organic matrix (~2.5 wt.%) controls the mineral deposit at a nanoscale (~97.5 wt.%).

* Corresponding author at: CNRS/INSU, ISTO, UMR 7327, 45071 Orléans, France. Tel.: +33 238 494 093; fax: +33 238 636 48.
E-mail address: xavier.bourrat@univ-orleans.fr (X. Bourrat).

Freshwater pearls show a biomineralisation defect that is characterised by a lack of lustre (or ‘milky’ pearl). Ma and Lee [2] were the first to show that this defect was connected to the allotropic transformation of carbonate: hexagonal vaterite forms in place of orthorhombic aragonite [3]. Vaterite is the less stable allotropic form of crystallised anhydrous calcium carbonate. The structural and chemical aspects of this defect have been studied in detail [4–7]. In addition, the presence of vaterite has been observed in the centre of good-quality pearls [8] and other molluscan tissues [9,10].

In the present work, the organic matrix of the milky pearls was extracted and analysed by means of various techniques that compared it to the matrix of healthy pearls. It was then used *in vitro* as an additive [11] in a controlled growth experiment with calcium carbonate and compared with the matrix of healthy pearls under the same conditions.

2. Experimental Section

2.1. Materials

We were provided with regular and milky pearls from Zhuji, China. *Hyriopsis cumingii* is the most commonly used ‘mussel’ for pearl culturing in the south of China (*Naiad* of the *Unionidae* family). The milky pearls were sorted based on visual criteria. Powder was obtained by crushing both types of pearls using an agate mortar and a sieve. The powder produced from crushing the regular pearl is made up of pure aragonite. The powder obtained from the milky pearls is a mixture of aragonite and vaterite. It was not possible to find pearls made entirely of vaterite to obtain a pure vaterite powder. The composition of the powders was verified by FTIR (Fig. 1). The main peak is the CaCO_3 ν_3 asymmetric stretching mode. This peak is split in two in the case of vaterite (1490 cm^{-1} and 1420 cm^{-1}). The third

peak (approximately 1470 cm^{-1}) is the ν_3 mode of aragonite. The same control measurement was obtained for all other peaks: ν_4 at 750 cm^{-1} , ν_2 at 877 cm^{-1} and ν_1 at 1088 and 1070 cm^{-1} . The spectra also showed the presence of weak bands that were attributed to the organic matrix: a wide band at 1630 – 1660 cm^{-1} and a finer one at 1557 cm^{-1} . These peaks are very likely the protein’s amide I (stretching mode of $\text{C}=\text{O}$ peptide bonds, mainly) and amide II (more complex coupling of $\text{C}=\text{N}$ stretching and the NH twisting modes).

The extraction of the organic matrix was conducted according to the flowchart in Fig. 2. The powder was mixed in a proportion of 25 g to 100 mL of Milli-Q water with stirring for 24 h. The water-soluble matrix (WSM) was obtained by filtration according to the protocol described by Pereira-Mouriès et al. [12]. The water insoluble residue was then decarbonated in a strong acid (HCl) using a pH metre bench set with a final point at $\text{pH}=4$. At these conditions, the powders were never decarbonated at a pH lower than 4. The strong HCl acid is preferred to acetic acid or to EDTA, which are known complexing agents. Filtration allowed for the separation of the acido-soluble organic matrix (ASM) from the acido-insoluble matrix (AIM).

2.2. Methods

Polished thin sections were examined under a cold cathode luminescence instrument provided by OPEA (Laboratoire d’Optique Electronique Appliquee, Vincennes France) mounted on a metallographic microscope (Olympus, BX-50). A cold cathode source electron gun was chosen for its ability to produce a stable electron beam (intensity-current fluctuations $<1\%$). Observations were carried out at an accelerating voltage of 15–20 keV and an operating current of 250–400 μA . Images were collected with a QUICAM Imaging Fast1394 digital camera in time integration mode using the Archimed Pro Microvision Instrument program. Spectra were obtained using a Carl Zeiss

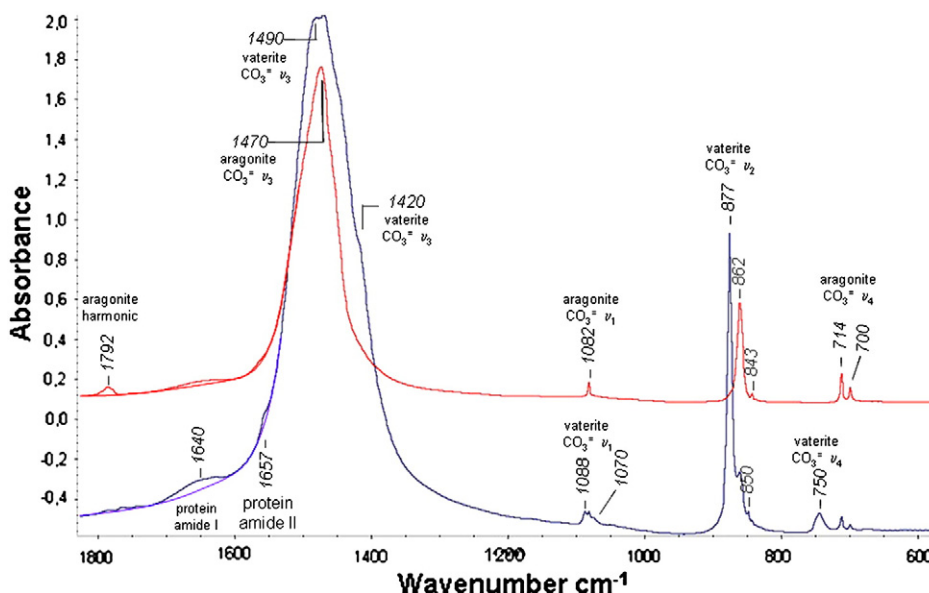


Fig. 1 – FTIR spectra of regular (red) and milky pearls (blue). Regular pearls exhibit pure aragonite spectrum; milky pearls exhibit both vaterite and aragonite allotropes. Note the presence of the main protein modes at the foot of the ν_3 carbonate peak.

Download English Version:

<https://daneshyari.com/en/article/1571380>

Download Persian Version:

<https://daneshyari.com/article/1571380>

[Daneshyari.com](https://daneshyari.com)