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Raman investigation of the pigment families in recent and fossil brachiopod shells

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ABSTRACT

Shells of the three subphyla of extant and extinct representatives of the phylum Brachiopoda display coloured patterns with diverse shapes and at different degrees. These colourations are readily visible in natural light but are best revealed under UV light for the fossils concerned. To identify these pigments, Raman spectroscopy has been used for the first time on brachiopod shells. The widespread identified pigments belong to the carotenoid family, best represented in all the animal kingdom, the second one concerns the melanin/melanin-like pigments and, surprisingly, additional molecules of the cytochrome family are revealed for the first time in one of the brachiopod shells studied. The putative functions of shell pigmentation, still under debate, are discussed.

1. Introduction

Brachiopods are marine benthic invertebrates, with a bivalved shell, present since the Lower Cambrian. Many extant species display a shell colouration, dispersed uniformly or present as patterns. Specimens of the three subphyla of the phylum Brachiopoda (Linguliformea, Craniiformea, Rhynchonelliformea) reveal this feature. The colouration is directly visible in natural light on shells of recent species. In the fossil world, colouration is more difficult to observe. The first descriptions of preserved colouration in fossil brachiopods date back to the middle of the 19th century [1–3]. The most ancient fossil brachiopods where residual colour patterns have been described go back to the Palaeozoic: the Ordovician [4], the Silurian [5], the Devonian (see [6,7] for partial reviews; see also [5,8,9]), the Carboniferous [2,6,7,10–12] and the Permian [7,8,13].

Shell colourations have also been observed on Mesozoic species: from the Triassic [14–19], the Jurassic [16] and the Cretaceous [16,18,19]. Finally, fossils from the Cenozoic also exhibited preserved colour patterns [16,20].

Whatever the fossil observed, the colouration under natural light revealed faded, even rub out. Similar observations emerged from mollusc shell analyses [21]. Nevertheless, Simpson [22] and, independently, Wagner [23] discovered the fluorescence ability of fossils and remains of vertebrates when excited by ultraviolet rays. This technique was then and is still commonly used for shell colouration studies on molluscs (see for example [24–26]). Regarding the brachiopods, this technique was used only very recently with similar results [19].

The next step of analysis was to tentatively identify the molecules responsible for these colourations. Raman spectroscopy was used for the first time in 1981 to allow identifying carotenoid pigments in a coral exoskeleton [27]. This technique was applied more recently on mollusc shells in a non-destructive manner [28,29]. On brachiopods, very little experiments have been performed to identify shell pigments. By using TLC (Thin Layer Chromatography) and mass spectrometry, Cusack et al. identified two carotenoids (canthaxanthin and astaxanthin) from the red shell of recent *Terebratella sanguinea* specimens (Rhynchonelliform) [30].

The aim of this work was to analyse the pigments involved in the colouration of the brachiopod shells from the three subphyla, on recent as well as on fossil species. Used for the first time on brachiopods, Raman spectroscopy has evidenced three families of pigments. Putative functions of shell pigmentation in brachiopods are discussed.

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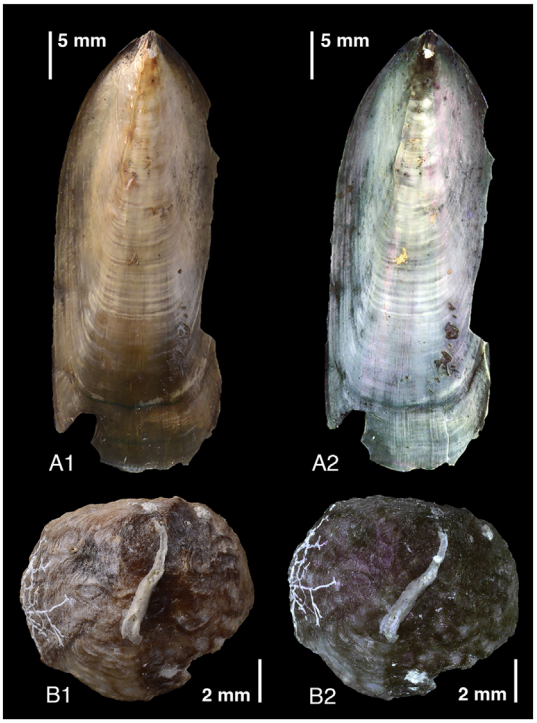

Fig. 1. A. *Lingula anatina* Lamarck, 1801 (Linguliformea Lingulidae). B. *Novocrania anomala* (Müller, 1776) (Craniiformea Craniidae). A1, B1: natural light pictures. A2, B2. UV light pictures emphasizing the growth lines and coloured radial patterns. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

2. Material and Methods

2.1. Brachiopod Specimens Analysed

Our work is based on the analysis of both extant (recent) and extinct (fossil) brachiopod species from different locations and stratigraphic ages. The different specimens analysed come from: the Zoothèque and Palaeontological collections of the Muséum National d'Histoire Naturelle (MNHN, Paris, France), the collections of Le Musée Vert, Musée d'Histoire Naturelle du Mans (MHNLM, Le Mans, France), the collections of Sorbonne Université (Paris, France) for the Triassic species, courtesy of members of the French Working Group on the Cretaceous (GFC) (University of Rennes, France), courtesy of brachiopod specialists from New-Zealand, D. Gaspard personal collections.

The extant species studied were:

- In the Linguliformea: *Lingula anatina* Lamarck, 1801 (Lingulidae), from the Japan coasts (MNHN Coll., n° MNHN.F.A69103).
- In the Craniiformea: *Novocrania anomala* Müller, 1776 (Craniidae), sampled from Gorringe bank (DW 37; 255–370 m), during the Seamount1 cruise (1987) (MNHN Coll., n° MNHN-IB-2014).
- In the Rhynchonelliformea: - *Notosaria nigricans* (Sowerby, 1846) (Notosariidae), from the New Zealand coasts (Tikoraki Point, 20 m depth) (MNHN Coll., n° MNHN.F.A69923), - *Neothyris lenticularis* (Deshayes, 1839) (Terebratellidae), from New-Zealand (Paterson Inlet, Steward Island, 15–25 m depth), (MNHN Coll., n° MNHN.F.A69930), - *Calloria inconspicua* (Sowerby, 1846) (Terebratellidae) from New Zealand (Tikoraki Point and Cape Wanbrow-Boatman Harbour at low-tide), (MNHN Coll., n° MNHN.F.A69929), - *Terebratella sanguinea* Leach, 1814 (Terebratellidae), from New Zealand (Doubtful Sound, 20 m depth), (MNHN Coll., n° MNHN.F.A69927), - *Terebratella haurakiensis* Allan, 1931 (Terebratellidae), from New-Zealand (Hauraki Gulf, 30–146 m depth), (MNHN Coll., MNHN.F.A69928), - *Frenulina sanguinolenta* (Gmelin, 1791) (Frenulinidae), from the Coral Sea (Chesterfield-Bellon Plate, 80 m depth), (MNHN Coll., n° MNHN.F.A60924) - *Dallinella occidentalis* (Dall, 1871) (Terebrataliidae), from Pacific Ocean (Californian coasts 100–205 m depth), (MNHN Coll., n° MNHN.F.A69925), - *Argyrotheca rubrocostata* Cooper, 1977 (Megathyrididae) from Caribbean Sea (26–55 m depth), (MNHN Coll., n° MNHN.F.A69926).

The extinct species studied were:

- In the Linguliformea: - *Lingulepis pinnaformis* Owen, 1852 (Obolidae), from St Croix Falls (Minnesota/Wisconsin, USA), (Mid-Upper Cambrian, ~500 My) (MNHN Coll., n° MNHN.F.A68135), -

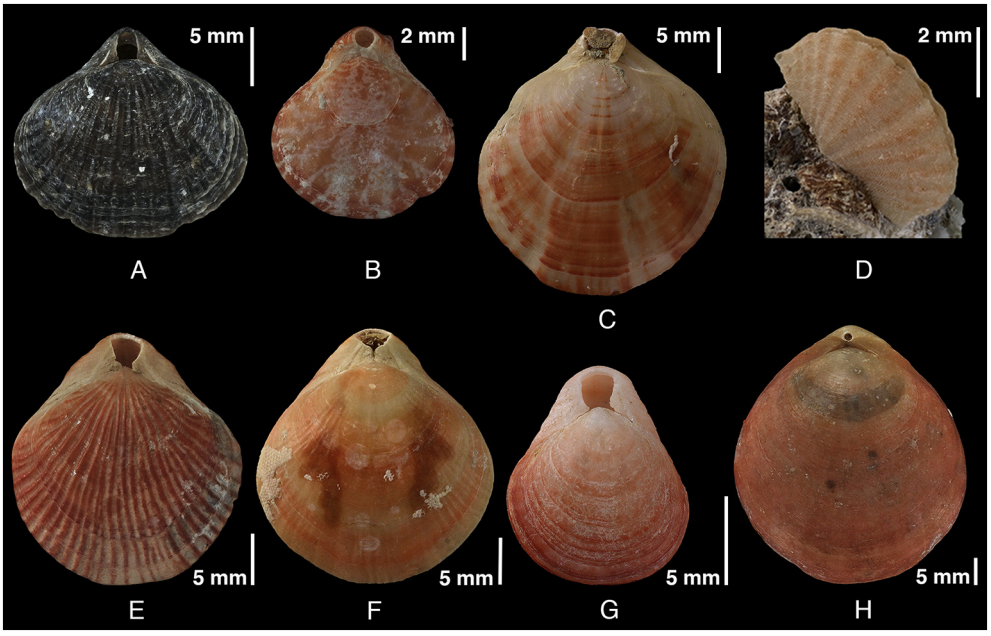

Fig. 2. Diversity of colouration and patterns in rhynchonelliform brachiopods (natural light pictures). A. *Notosaria nigricans* (Sowerby, 1846). B. *Frenulina sanguinolenta* (Gmelin, 1791). C. *Dallinella occidentalis* (Dall, 1871). D. *Argyrotheca rubrocostata* Cooper, 1977, E. *Terebratella sanguinea* Leach, 1814, F. *Terebratella haurakiensis* Allan, 1931. G. *Calloria inconspicua* (Sowerby, 1846). H. *Neothyris lenticularis* (Deshayes, 1879). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)