M9 MOLECULAR STRATIGRAPHIC ANALYSIS WITH RAMAN SPECTROSCOPY OF THE SHELL OF A MUSSEL

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Abstract
Two different cristallographical forms of calcium carbonate (aragonite and calcite) has been identified in mussels with Raman spectroscopy.
Keywords: Raman spectroscopy, shells, pigments, calcium carbonate

INTRODUCTION

The main objective of this work is to analyze the materials (colored or not) that compose a mussel´s shell. In order to get this objective a meticulous stratigraphic analysis has been carried out with Raman spectroscopy. The fundamental reason to use Raman spectroscopy is because this analytical technique provides information about molecular composition and crystal structure of the compounds in a non-destructive and unambiguous way. This molecular knowledge of the materials that form this kind of sea shell can be useful to understand the formation and growth biologic mechanisms of the shells of molluscs.

STRATIGRAPHIC ANALYSIS WITH RAMAN SPECTROSCOPY

The most remarkable of this investigation is the discrimination of two different crystal structures of calcium carbonate in a mussel, this is to say, aragonite in the substrate and calcite in the blue areas. In the figure 1, the cross-section photography of this mussel´s shell is shown. The corresponding Raman spectra obtained in the points (a) to (f) appear in the figure 2.

The aragonite ($CaCO_3$, orthorrombic), with bands at 152, 179, 205, 701 and 1082 cm-1, has been identified (practically isolated or combined) as the principal compound of the biologic substrate in the mussel´s shell (spectra a, b and c). The Raman bands at 1013 and 1093 cm-1 in the spectra (b)-(f) can be attributed to a certain kind of blue pigment (polyene)[1,2]. Its concentration increases progressively at the same time that the concentration of aragonite decreases.

However, with this rise in concentration of the blue pigment, also a structural change (crystallographic) of the calcium carbonate in the substrate is observed. In the points (d) and (e) of the cross-section (Fig. 1) the Raman spectra (d) and (e) were obtained (Fig. 2). It is possible to identify, in addition to aragonite, other crystallographic form of calcium carbonate, this is, calcite ($CaCO_3$, trigonal), which fundamental bands are located at 154, 281, 711 and 1084 cm-1. The band at 1084 cm-1 is masked due to the more intense band at 1093 cm-1 corresponding to the blue pigment (spectra d, e and f). Finally, in the total blue layer, the obtained spectrum (f) shows how the calcite appears as the fundamental compound mixed with the blue pigment instead of the aragonite, which presence has disappeared.

CONCLUSIONS

The fundamental compounds of a shell can easily be identified thanks to Raman spectroscopy. However, in the particular case of a mussel, we note that two different crystallographic forms of calcium carbonate coexist together: aragonite in the general substrate and calcite in the blue areas. This fact, perhaps, helps to understand the formation process of the shell of this mollusk.

ACKNOWLEDGEMENTS

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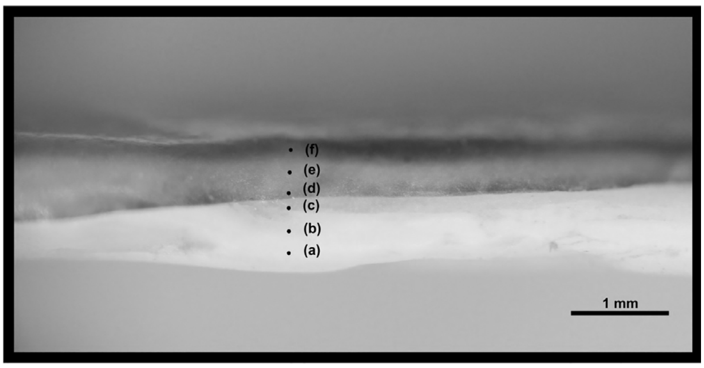

Fig. 1. Photography of a mussel´s shell cross-section

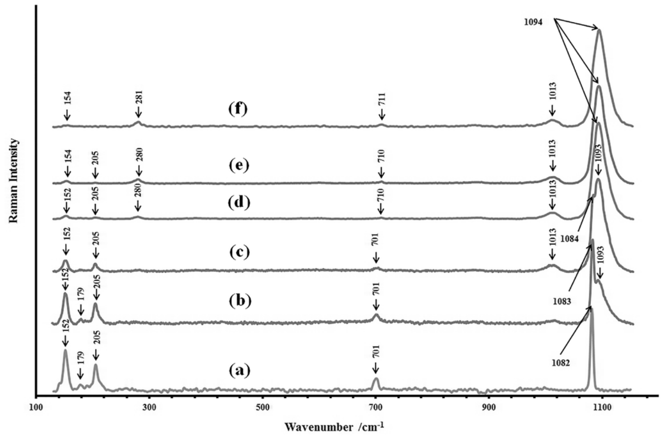

Fig.2. Raman spectra obtained at different layers (a-f) of the cross-section of the mollusk: Raman spectrum of aragonite (a); Raman spectra of aragonite mixed with the blue pigment (b and c); Raman spectra of an aragonite, blue pigment and calcite mixture (d and e); and Raman spectrum of calcite mixed with the blue pigment (f).