THE STUDY OF ANCIENT COOKING TECHNIQUES OF MOLLUSK SHELLS FROM TIERRA DE FUEGO BY SEM-EDX AND RAMAN SPECTROSCOPY

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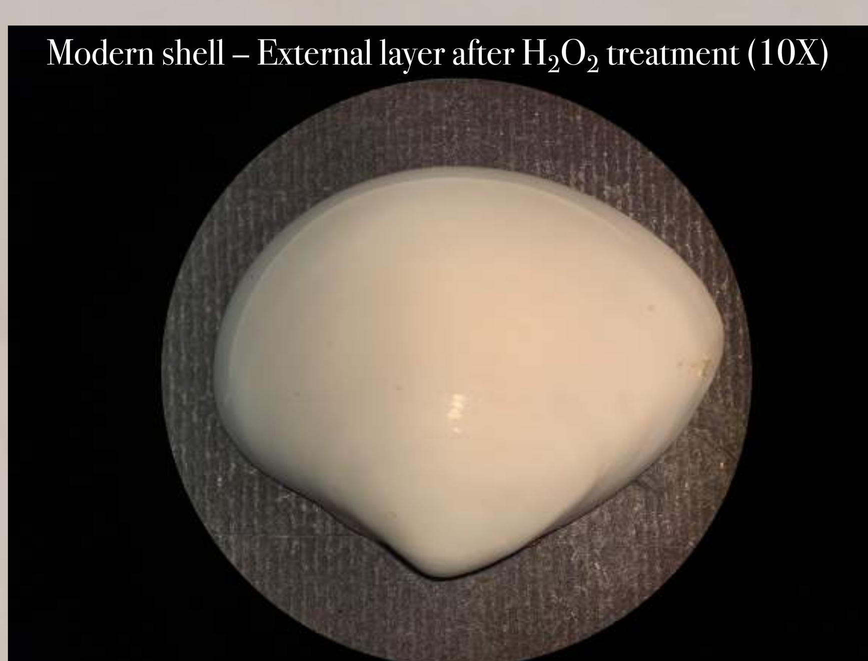
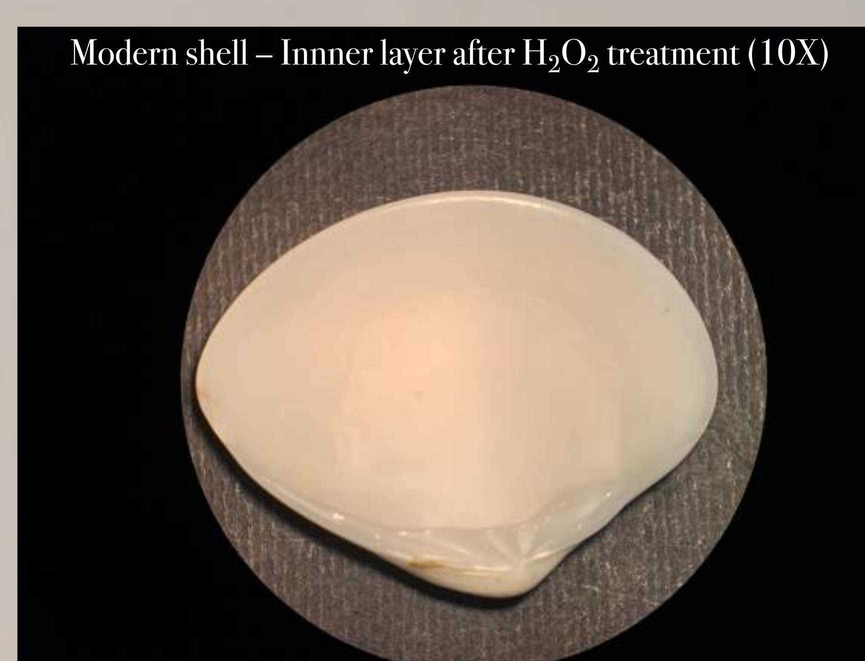
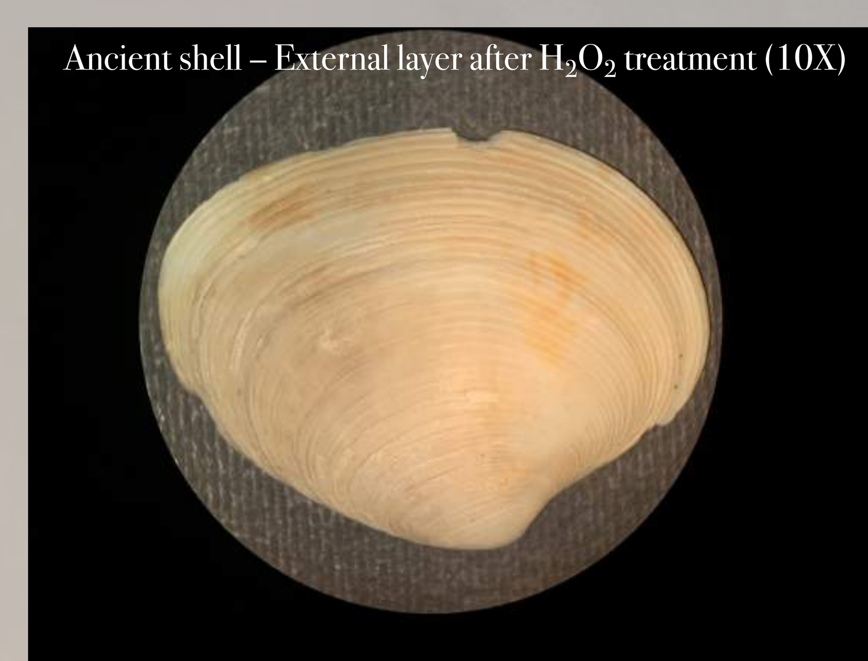
Seafood has always been an important component of human nutrition since ancient times. For example, the study of mollusk shells, which represent the residue of human consumption, could reveal traces left by cooking, thus is very interesting because it can provide useful anthropological and cultural indications regarding ancient populations. In fact, temperature could change the structures and properties of shells and the study of this changes can be a way for investigating the cooking techniques, enlightening the cultural habits and the technological capabilities of ancient populations.
As a case study, SEM-EDX and Raman spectroscopy investigations were carried out on shells of modern bivalve mollusks, before and after treating them at different temperatures and times on flame.
Results were then compared to those obtained by analysing by means of the same techniques some samples of ancient mollusks of the same family, coming from Tierra de Fuego and dating back to a period of about 5000-6000 years before the present, as evaluated using the radiocarbon method.
Analyses were carried out after the removal of the organic parts of the shells by means of H_2O_2 treatment .

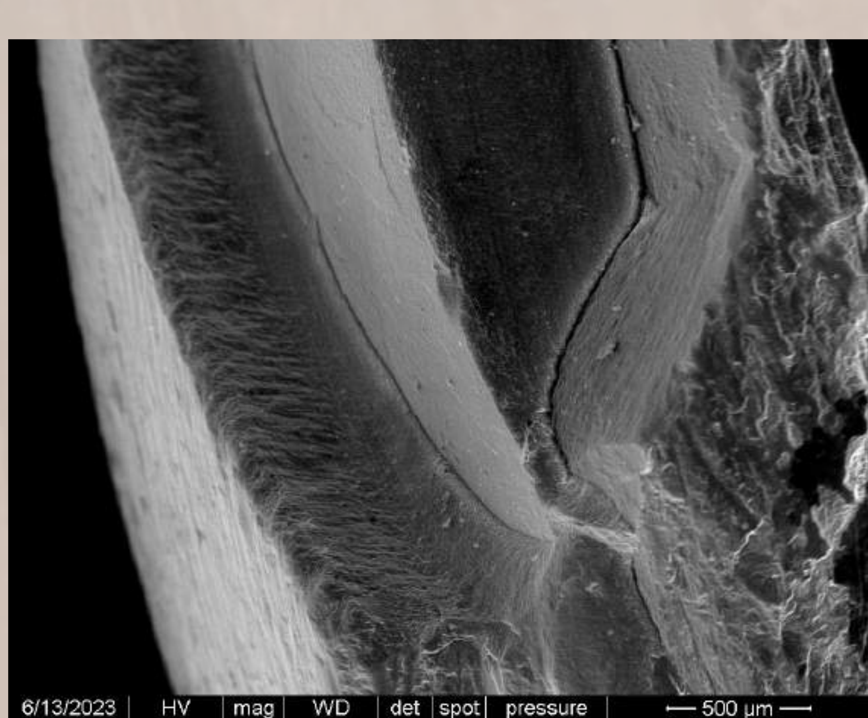

Modern shell – External layer after H_2O_2 treatment (10X)

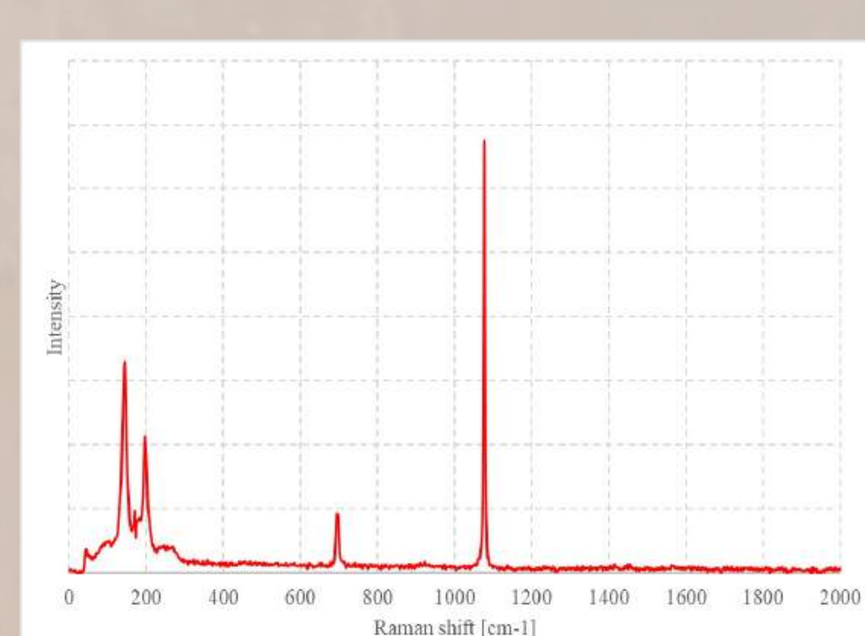

Modern shell – Innner layer after H_2O_2 treatment (10X)


Ancient shell – External layer after H_2O_2 treatment (10X)


Ancient shell – Inner layer after H_2O_2 treatment (10X)

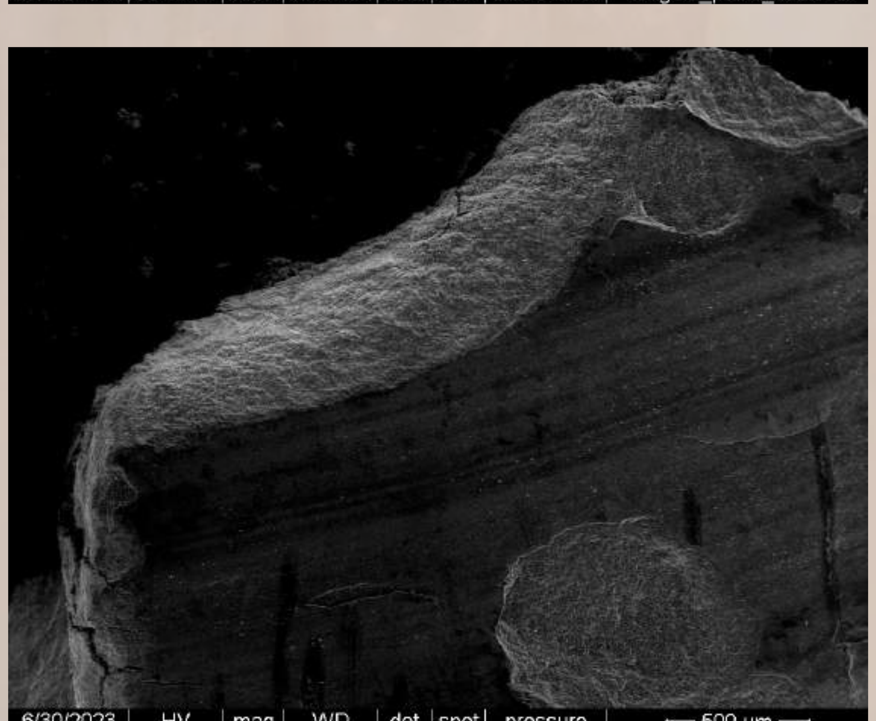
Inorganic materials are used by living organisms in an innumerable number of cases and for the most diverse purposes, including uses such as protection, defence, attack and structures for resistance to loads and mechanical stresses. The inorganic part of many invertebrates, especially marine, but not only, including mollusks and corals use carbonates to build the hard parts of their body.
To achieve the intended purpose of their function, these inorganic materials are organized and structured at the microscopic and sometimes even sub-microscopic level with absolute precision, due to the driving force of evolution rules. Sometimes, these biomineralized inorganic materials have different physical and chemical properties from their counterparts of geological origin. For example, calcium carbonate can be found in different polymorphs: Calcite, which is most stable at room temperature and pressure, Aragonite. Aragonite is normally kinetically stable and does not transform into the more stable Calcite at room temperature, however a phase transition occurs when heated. It is interesting to note that in some cases for samples of biological origin it has been reported that this transition temperature is different.



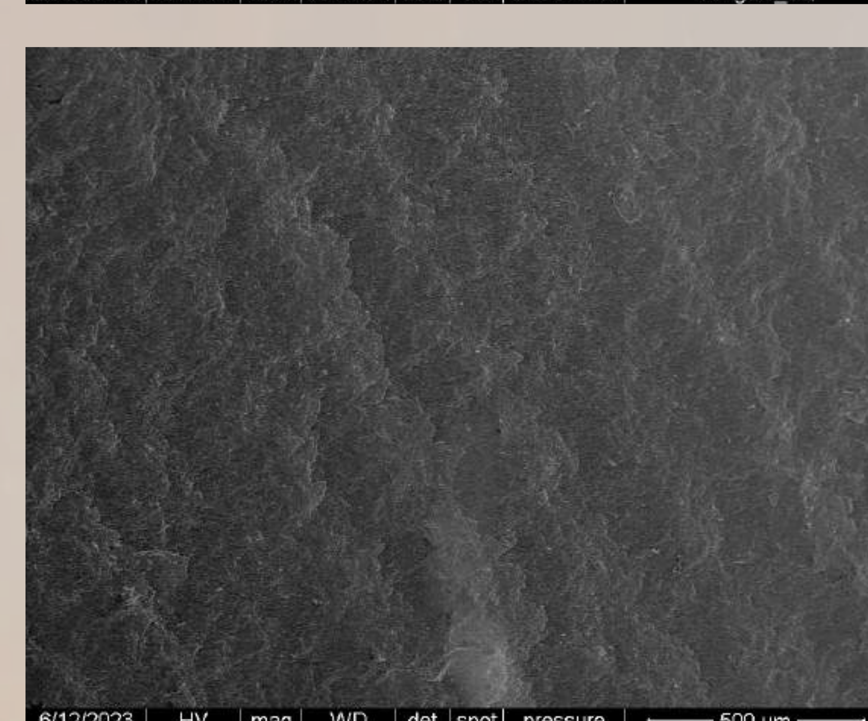


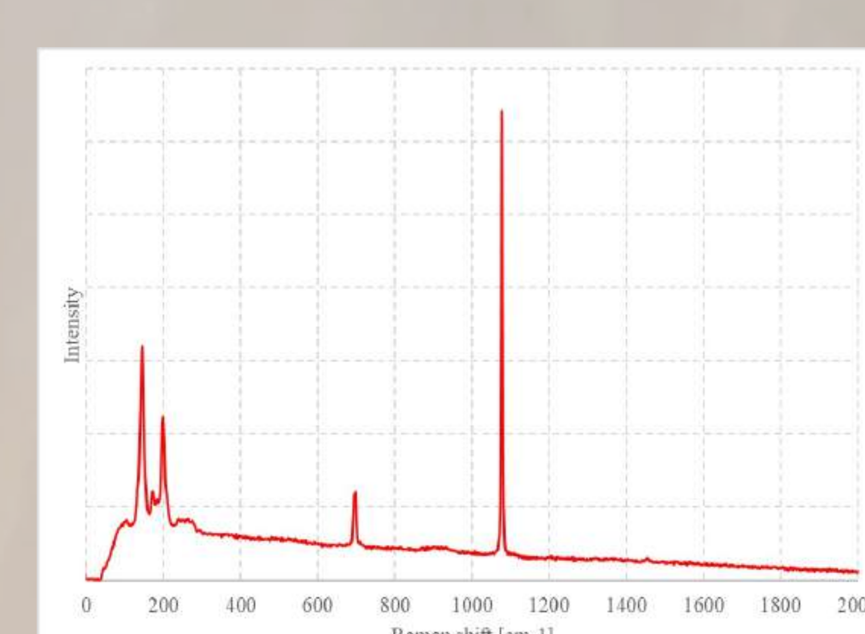
Modern shell inner layer: pure Aragonite

Ancient shell inner layer before H_2O_2 treatment: Aragonite

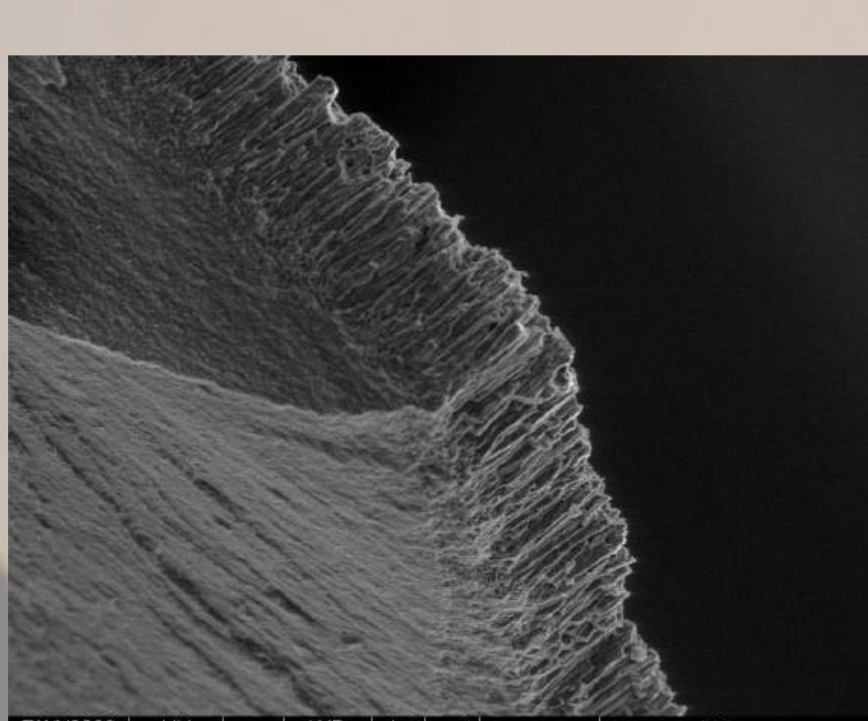


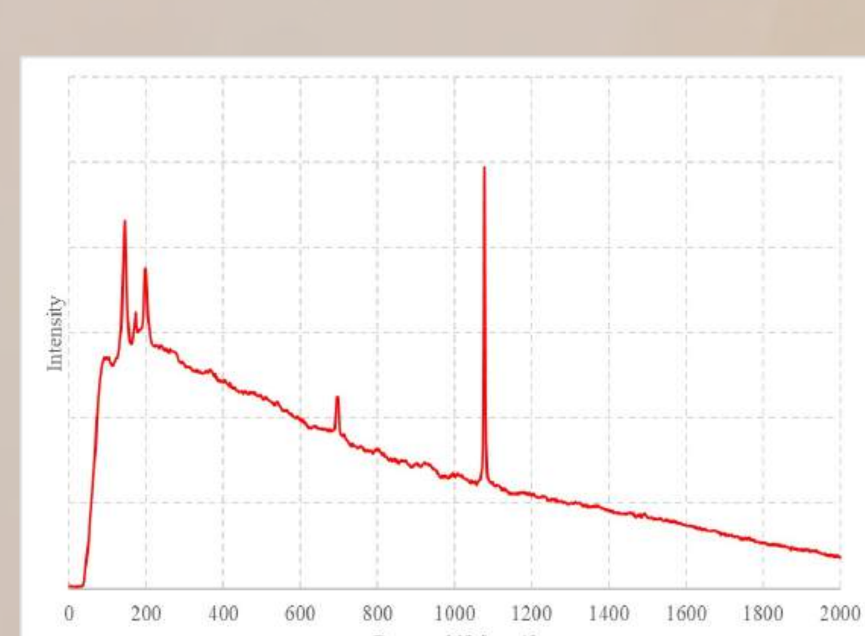
Modern shell inner layer after 1 min fire: Aragonite and Calcite





Ancient shell inner layer: Aragonite





Modern shell inner layer after 1 hour at 350°C: Aragonite and traces of Calcite

Conclusions

The chemical and morphological analysis of the shells of the mollusks considered has revealed that they are mainly made up of Aragonite and organic components. There are differences in the morphology and orientation of individual crystallites, but not in their composition.
The transition between the two polymorphs can be used to study the modifications that can occur as a result of any heating treatment and this allows us to know some cultural uses of ancient peoples.
A modest heating, either directly through a flame or controlled, induces the transition to Calcite, that can be found in small amounts. Interestingly, in ancient mussels, Calcite does not seem to be present and this seems to exclude any type of cooking.

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