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HEAT-INDUCED MODIFICATION OF MARINE SHELLS USED AS PERSONAL ORNAMENTS AT THE PREHISTORIC SITE OF FRANCHTHI CAVE, GREECE: FIRST RESULTS OF A MULTIANALYTICAL APPROACH

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ABSTRACT
The prehistoric site of Franchthi Cave located in the south-eastern Argolid in Greece yielded an exceptionally rich collection of personal ornaments. A reassessment of this category of material culture by two of us (CP and MV) led to the hypothesis that one type of personal ornaments, i.e. marine shell beads belonging to the species Cyclope neritea, were intentionally heated to change their natural whitish colour to black. In order to identify possible diagnostic criteria for intentional heating based on the physical properties of the shells we submitted two modern Cyclope neritea shells, one of which unmodified, the other experimentally blackened through heating, and two archaeological specimens, one presenting a natural whitish colour, the other black, to complementary analytical methods: optical (OM) and scanning electron microscopy coupled with an X-ray analysing system (SEM-EDX), infrared (FT-IR) and microRaman spectroscopy as well as differential scanning calorimetry (DSC). Results show that heated shells can be identified based on their microstructure and chemical composition and that the black archaeological shell positively matches the modern shell blackened through heating. Identification of the limited conditions, in which blackening through heating occurs, further supports a special heat-treatment for Cyclope neritea shells at Franchthi Cave.

INTRODUCTION
Franchthi Cave is a prehistoric site located in the South-eastern Argolid which yielded an over 11 meters stratified sequence of deposits spanning from the early Upper Palaeolithic to the Final Neolithic [2, 4]. One of the materials used as personal ornaments at this site is composed of seashells belonging to the species *Cyclope neritea*. The shell of this species has a diameter of ca. 1 cm, the dorsal side is orange-pastel-coloured and the ventral side ivory-coloured. An ongoing reassessment of the personal ornaments of Franchthi Cave by two of us (CP and MV) reveals that besides naturally bright coloured archaeological shells (fig. 1b), other specimens display a much darker colour (fig. 1c,d) suggesting they might have been blackened through heating [5]. The aim of this study is to identify possible diagnostic criteria for intentional heating of the shells through the use of a variety of analytical methods that allow characterising their micromorphology, structure and chemical composition by limited sampling.

MATERIAL AND METHODS
In order to identify possible diagnostic criteria for intentional heating based on the physical properties of the shells we submitted two modern *Cyclope neritea* shells, one of which unmodified (fig. 1a), the other experimentally blackened through heating (fig. 1c) and two archaeological specimens, one presenting its natural whitish colour (fig. 1b), the other black (fig. 1d), to complementary analytical methods.

Optical (OM) and electron microscopy coupled with an X-ray analysing system (SEM-EDX) were used for observation of the shells from the macroscopic to the micrometer scale. Fourier transform infrared spectroscopy (FT-IR) and microRaman spectroscopy were performed for structural investigations of mineral phases and to determine the presence of organic compounds. Additionally, differential scanning calorimetry (DSC) was used to observe mineral phase transitions upon heating. Finally, a protein indicating method was used to evidence the presence of proteins in sample cross sections.

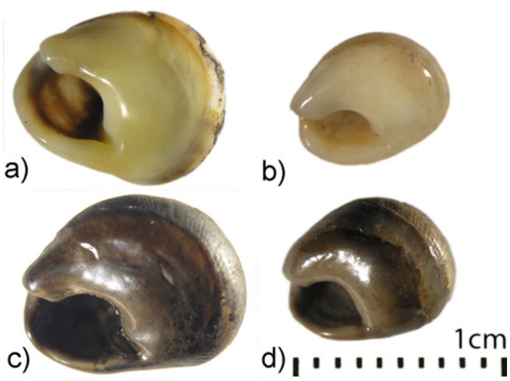

Fig. 1: Ventral side of Cyclope neritea shells a) unmodified modern shell b) white archaeological shell, c) modern shell experimentally blackened through heating, d) black archaeological shell.

Optical Microscopy (OM)

A Nicon SMZ-10A equipped with a Coolpix MDC Lens camera was used to observe the colour and the surface of the entire shells as well as the structure and colour of cross sections. Maximum magnification was of x49. The observation of the entire shells did not need preparation in contrast to that of the cross sections. For the preparation of a cross section a sample fragment is inlayed in a resin and cut with a diamond sow; afterwards the cut surface is polished.

Scanning Electron Microscopy Coupled with an Energy Dispersive X-ray Analysing System (SEM-EDX)

A Philips XL 30 CP SEM with a Si(Li) detector equipped with an ultrathin window and the Link Isis 300 EDX system was used for the observations of shell cross sections at microscale. All observations and measurements were carried at 20 kV. Samples of isolating material such as shells are metallised on the surface with carbon to permit charge evacuation.

Protein Indication Method

The reaction of Amide Black on cross sections allows visualizing proteins in a sample. A drop of the reagent is added on the cross section of a sample. After a minute the drop is removed with a tissue and the cross section rinsed with a drop of water. The stained zones indicate the presence of proteins.

The used reagent (NA_2) is composed of 1 g of colorant for 450 cm^3 of acetic acid N, 450 cm^3 of sodium acetate (0,1N), 70 cm^3 of glycerine and 30 cm^3 of sodium phosphate (0,2N). The pH-value of the reagent is 3.6 [3].

Fourier Transform Infrared Spectroscopy (FT-IR)
A Perkin Elmer Spectrometer Spectrum 2000 was used for the analysis. It is equipped with a DTGS-detector, a separator and a CsI window. The measuring range lies between 6000 cm^{-1} and 250 cm^{-1}. Samples are prepared as KBr pellets and analysed in transmission mode. For the preparation of the KBr pellets, 1 mg of sample and KBr are mixed in form of powders at a ratio of 1:100 and pressed at 8t/cm^2. The detection limit is ca. 5 wt.%.

MicroRaman Spectroscopy
Raman spectra were collected at the microscope output of a LabRam Infinity micro-spectrometer (Jobin-Yvon) using a laser excitation at 532 nm. The beam diameter is of about 2 µm. A magnification of x50 was used for analysis. Analysis was realised on entire samples as no sample preparation is necessary for Raman spectroscopy.

Differential Scanning Calorimetry (DSC)
A Netzsch STA 409EP was used for DSC on sample fragments. The measurements were realized between 20°C and 500°C with a heating of 10°C /minute. Phase transitions upon heating can be detected by a variation of the DSC signal.

RESULTS
SEM observation of cross sections shows a difference in the microstructure of white and black shells. Modern and archaeological white shells are constituted of five well distinguishable layers (fig. 2).

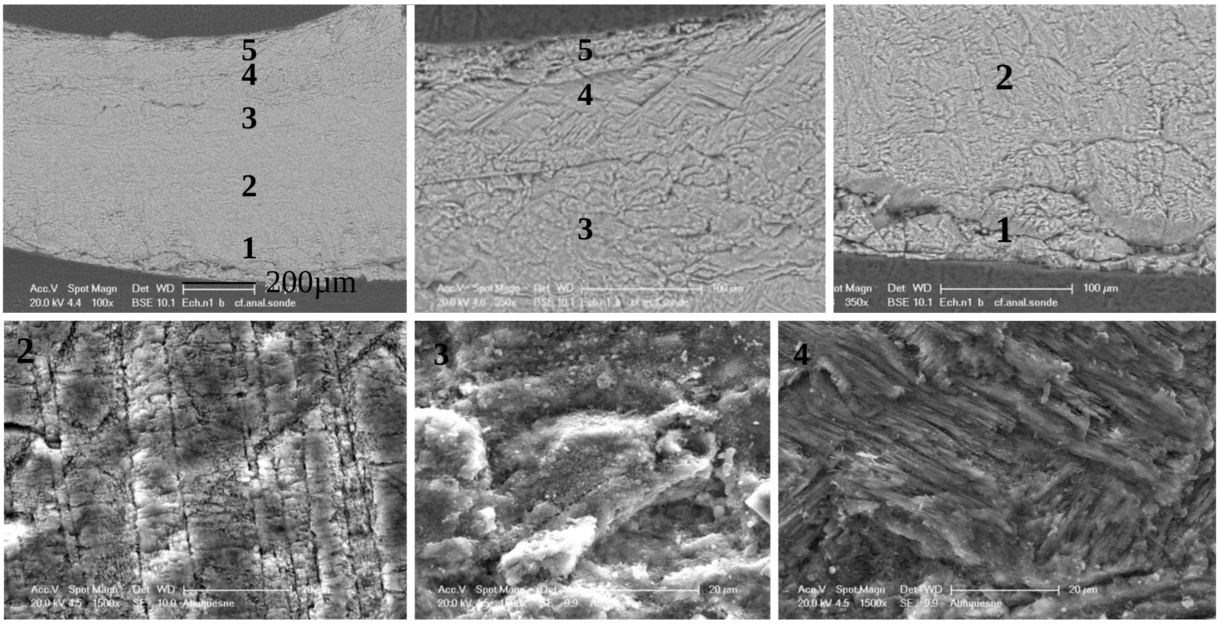

Fig. 2: SEM observation of cross sections of a white modern shell reveals a microstructure composed of five layers. Numbers 1 to 5 in the micrographs correspond to the respective layers described in the text.

The outermost layer with a thickness of ~50 µm does not show a well organised assembly of crystals and therefore seems to be altered (fig. 2 n°1). The following layer of ~300 µm presents a structure of interweaved lamellas of 5-15 µm thickness, which run perpendicular to the surface of the shell (fig. 2 n°2). Underneath lies a layer of 100 µm thickness, consisting of a conglomerate of crystals of different sizes (fig. 2 n°3). The fourth layer of ~50 µm has a structure of crossing lamellas (fig. 2 n°4). The last inner layer of 30 µm seems altered again (fig. 2 n°5). In contrast, the microstructure of the archaeological and experimentally heated black shells is constituted of only one layer showing elongated crystals (fig. 3).

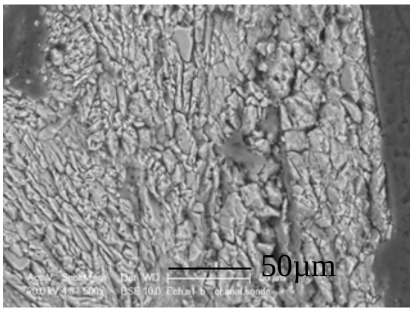

Fig. 3: SEM observation of a black modern shell reveals a single layer composed of elongated crystals.

FT-IR and microRaman show that black and white shells contain a different polymorph of calcium carbonate. White shells contain mostly aragonite (fig. 4), a polymorph formed in the biomineralisation process of shells, whereas black shells contain mostly calcite, the more stable polymorph of calcium carbonate under ambient conditions. The microRaman spectrum of the black shells (fig. 5) shows in addition to the calcite bands peaks of a carbonized product (amorphous carbon).

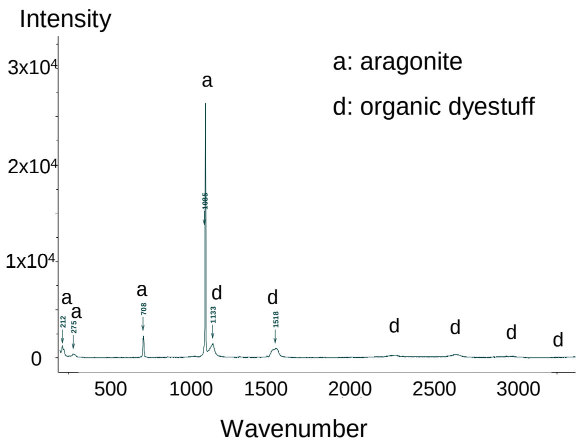

Fig. 4: MicroRaman spectrum of a bright recent shell: aragonite and an organic dyestuff are detected.

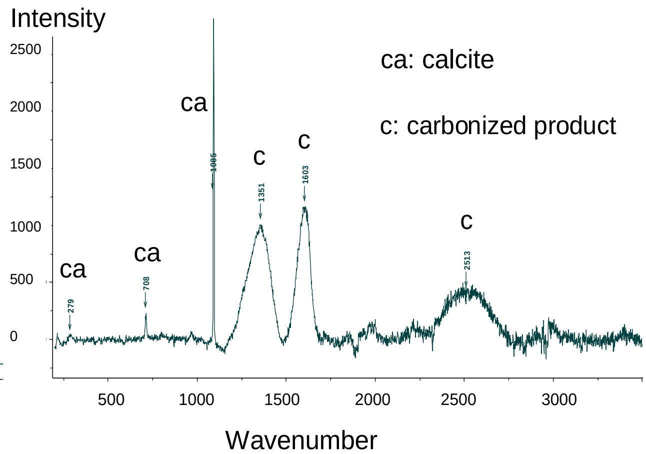

Fig. 5: MicroRaman spectrum of the black archaeological shell: calcite and a carbonized product are detected.

The elemental composition of the shells as determined by SEM-EDX shows that for both, black and white shells, the main elements are Ca, O and C. In addition, slight quantities of P, Na, Al, S and Cl were detected in all samples. Black and white shells differ however in their ratio of C to Ca. The C to Ca ratio in the white shells is low, whereas it is elevated in the black ones, indicating a carbon enrichment in the black shells.

DSC measurement of a fragment of a white modern shell fragment reveals that a mineral phase transformation takes place at about 250°C (fig. 6). Structural analysis of the sample before and after heating to 250°C shows that this phase transformation corresponds to the aragonite to calcite transition.

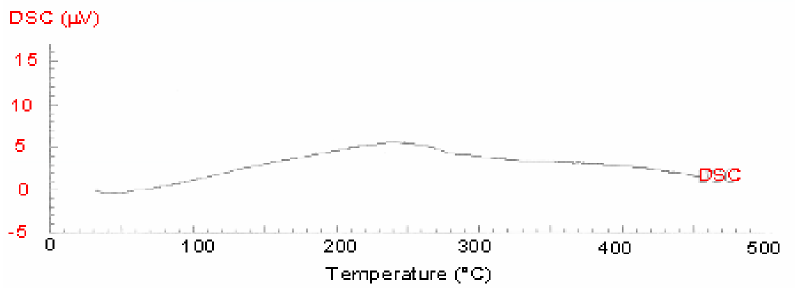

Fig. 6: DSC diagram: phase transformation at about 250°C is visible

To evidence the presence of inherent organic shell compounds, a protein indication method (amide black) was used on cross sections of the different samples (fig. 7) Proteins are observed in the layer 4 of the white modern shell (fig 7b), whereas there are no proteins found in the modern heated shell.

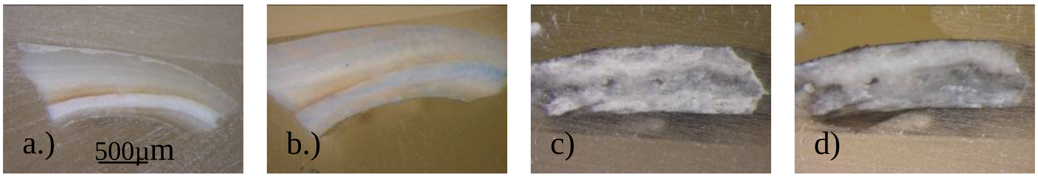

Fig.7: Protein indication test on cross sections, proteins are indicated in blue:
(a) white modern shell b) white modern shell with indicator c) heated modern shell
d) heated modern shell with indicator.

DISCUSSION AND CONCLUSION

Obtained results show that shells submitted to heating can be identified on the basis of their microstructure and chemical composition. Natural *Cyclope neritea* shells are characterised by five distinct microstructural layers that are mainly composed of the aragonite polymorph of calcium carbonate [6]. In contrast heated *Cyclope neritea* shells display only one structural layer that is mainly composed of the calcite polymorph of calcium carbonate and are further characterised by the presence of a relative high amount of amorphous carbon. Observation of the former characteristics on the white archaeological shell indicates that this shell was used as such and did not suffer demonstrable diagenetic alterations while buried in the ground. Analysis of the black archaeological shell indicates that it was modified through heating as it displays the same characteristics as the modern heated specimen [1,7].

Results further indicate that the black coloration can only be achieved by heating under limited conditions. As indicated by the DSC analysis, the minimal temperature necessary to transform aragonite into calcite is 250°C. However, this mineral phase transition does not explain in itself the blackening of the shell. As indicated by the Raman and EDX-analyses the black colour is due to a relatively high amount of amorphous carbon adhering to the surface of the shell. Amorphous carbon is a carbonized product released when organic material is burned. In a regular open fire place, characterised by an oxidising atmosphere, carbon originating from organic matter would escape in form carbon dioxide in the atmosphere. Only reducing conditions would allow the formation of a black carbonised product staining the shells. This suggests that black archaeological shells received a special heat-treatment by the prehistoric occupants of the site. However, in order to demonstrate that these conditions could not occur accidentally, other contextual data, which will be developed in a forthcoming publication by the authors, have to be brought in.

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BIBLIOGRAPHY

1. W. D. Carlson « The polymorphs of $CaCO_3$ and the aragonite –calcite transformation » in: R. J. Reeder (ed.) Carbonates: Mineralogy and Chemistry, Reviews in Mineralogy; Vol. 11, Mineralogical Society of America 1983, 191-225.
2. T.W. Jacobsen & W. R. Farrand « Franchthi Cave and Paralia. Maps, Plans and Sections ». in: Excavations at Franchthi Cave, fasc. 1, Indiana University Press, Bloomington / Indianapolis, 1987, 33p. + pl.h.t.
3. E. Martin « Application des tests sur coupes minces à l'identification des émulsions dans les liants de peinture » Annales du laboratoire des musées de France, 1977, 23-29.
4. C. Perlès « Long-term perspectives on the occupation of the Franchthi Cave ». in: G. Bailey, A. Adam, E. Panagopoulou, C. Perlès et K. Zachos (eds), The Palaeolithic archaeology of Greece and adjacent areas: proceedings of the ICOPAG Conference, Ioannina, September 1994, British School at Athens, Studies 3, London, 1999, 311-318.
5. C. Perlès « The Mesolithic at Franchthi: an overview of the data and problems » in: Galanidou, N. and Perlès, C. (eds.), The Greek Mesolithic, British School at Athens, BSA Series n°10, 2003, 79-89.
6. J. Philippon « Structure et composition minéralogique de la coquille de gastropodes actuels et fossiles », 1974, 131.
7. J. Stolarksi, R. Przeniosto, M. Mazur, M. Brunelli « High resolution synchrotron radiation studies on natural and thermally annealed scleractinian coral biominerals » Journal of Applied Crystallography 2007, 40, 2-9.

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