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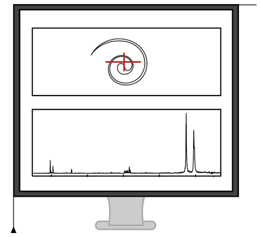
LIBS Mapping of Mg/Ca ratios in marine mollusc shells V.1



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Niklas Hausmann[1], Amy Prendergast[2], Andreas Lemonis[3], Jana Zech[4], Patrick Roberts[4], Panagiotis Siozos[4], Demetrios Anglos[3]

[1]Foundation for Research and Technology-Hellas, Institute of Electronic Structure and Laser;
[2]University of Melbourne, School of Geography; [3]University of Crete, Department of Chemistry;
[4]Max Planck Institute for the Science of Human History

Niklas Hausmann
University of York

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Protocol status: In development
We are still developing and optimizing this protocol

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Abstract

Elemental analysis of biogeochemical archives is an established technique used to study climate in a range of applications, including ocean circulation, glacial/interglacial climates, and anthropogenic climate change. Data from mollusc archives are especially important because of their global abundance and sub-annual resolution. Despite this potential, they are underrepresented among palaeoclimate studies, due to enigmatic physiological influences skewing the elemental record. Understanding the patterns behind these influences will improve data interpretation and lead to the development of new climate proxies. Here, we show for the first time that extensive spatial mapping of multiple mollusc specimens using Laser Induced Breakdown Spectroscopy (LIBS) across a wider region can resolve enigmatic patterns within the elemental record caused by physiological influences. 2D elemental (Mg/Ca) maps of whole limpet shells (Patella caerulea) from across the Mediterranean revealed patterns of variability within individual mollusc records as well as within isochronous parts of specimens. By registering and quantifying these patterns, we established previously uninterpretable correlations with temperature ($R2 > 0.8$, $p < 0.01$). This outcome redefines the possibilities of accessing sub-annual climate proxies and presents the means to assess annual temperature ranges using oxygen isotope analysis requiring only 2 samples per shell.

Materials

STEP MATERIALS

Water

Ethanol

Protocol materials

Water Materials, Step 1

Ethanol Materials, Step 1

Sample preparation

1

Equipment

ISOMET 1000 Precision Saw	NAME
Saw	TYPE
Buehler	BRAND
11-2180	SKU
Using a Buehler Diamond Wafering Blade (Series 15LC Diamond No. 11-4276)	SPECIFICATIONS

- Section shells at the hinge and along the direction of growth. If necessary remove non-hinge parts of the section to reduce the overall size.
- Select the 'better' side of the two sections and clean off with

Water

and

Ethanol

- Prepare a rudimentary holder ('Vesselheim') using crumpled up aluminium foil (and cradle the shell half into it, so that the section is facing up and is near-horizontal

- Place the sample into the centre of the xyz stage

Equipment	
XYZ Stage	NAME
Translation stage	TYPE
STANDA	BRAND
(Standa 8MT200-100DCE)	SKU

Laser specifications

2

Our LIBS system used a q-switched Nd:YAG laser operating at 1064 nm (infrared). Pulse duration was 10 ns and each pulse had an energy of ~10 mJ.

Equipment	
new equipment	NAME
Q-switched Nd:YAG Laser	TYPE
Spectron Laser Systems	BRAND
n/a	SKU

Using an objective lens for infrared light, with a magnification of 10, we focused the laser beam onto the surface of the shell, creating an in-situ plasma plume and sampling an area of ~50μm.

Following irradiation, the plasma plume emitted light which we collected using a quartz fibre, which guides the light into a spectrograph using a 600 l/nm grating.

Equipment

LMH-10x	NAME
objctive lens	TYPE
Thorlabs	BRAND
LMH-10X-1064	SKU
https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=4243&pn=LMH-10X-1064	LINK

The light exits the spectrograph onto the sensor of an ICCD, which is synchronized with the Q-switch of the laser and gated using a digital delay pulse generator (DG535, Andor Technology). We used a delay of 500 ns and a gating of 1000 ns.

Equipment

Czerny-Turner Spectrograph	NAME
TRIAX320	TYPE
Jobin Yvon	BRAND
n/a	SKU

Using a customised setup in LabView, we measured the peaks of the spectrum measured by the ICCD using the peak at 279.553 nm for MgII and 315.887 nm for CaII. The resulting ratio was associated with the location of the xyz-stage and saved as a csv file.

Equipment

DH520-18F	NAME
ICCD	TYPE
Andor Technology	BRAND
n/a	SKU

Software	
LabView	NAME
National Instruments	DEVELOPER

Data plotting

3

The xy- values of the csv file were used to plot a point cloud in QGIS. Each point was then coloured by their respective Mg/Ca intensity ratio, resulting in an elemental map of the shell section.

Software	
QGIS	NAME