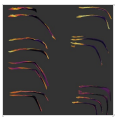

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Working

LIBS Mapping of Mg/Ca ratios in marine mollusc shells

Version 2

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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.

PROTOCOL STATUS

Working

We use this protocol in our group and it is working

STEPS MATERIALS

NAME	CATALOG #	VENDOR
Water		
Ethanol		

Sample preparation

1

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

- 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

XYZ Stage
Translation stage
STANDA (Standa 8MT200-100DCE)

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.

Q-switched Nd:YAG Laser
Spectron Laser Systems n/a

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.

LMH-10x
objctive lens
Thorlabs LMH-10X-1064

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.

Czerny-Turner Spectrograph
TRIAX320
Jobin Yvon n/a

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.

DH520-18F
ICCD
Andor Technology n/a

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.

LabView
by National Instruments

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.

QGIS