

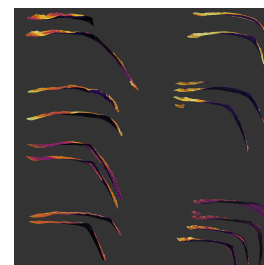
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Version 2

LIBS Mapping of Mg/Ca ratios in marine mollusc shells V.2

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Protocol status: Working

We use this protocol and it's working

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Keywords: data from mollusc archive, extensive spatial mapping of multiple mollusc specimen, mollusc archive, multiple mollusc specimen, ratios in marine mollusc shell, individual mollusc record, elemental analysis of biogeochemical archive, enigmatic patterns within the elemental record, marine mollusc shell, biogeochemical archive, palaeoclimate study, underrepresented among palaeoclimate study, isochronous parts of specimen, elemental record, elemental analysis, oxygen isotope analysis, using oxygen isotope analysis, including ocean circulation, laser induced breakdown spectroscopy, using laser induced breakdown spectroscopy, interglacial climate, maps of whole limpet shell, global abundance, climate, ocean circulation, new climate proxy, uninterpretable correlations with temperature

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 ($R^2 > 0.8$, $p < 0.01$). 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

 Ethanol

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

Equipment

XYZ Stage

NAME

Translation stage

TYPE

STANDA

BRAND

(Standa 8MT200-100DCE)

SKU

- Place the sample into the centre of the xyz stage

Laser specifications

2

Equipment

new equipment

NAME

Q-switched Nd:YAG Laser

TYPE

Spectron Laser Systems

BRAND

n/a

SKU

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

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

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.

Equipment

Czerny-Turner Spectrograph	NAME
TRIA320	TYPE
Jobin Yvon	BRAND
n/a	SKU

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

DH520-18F

NAME

ICCD

TYPE

Andor Technology

BRAND

n/a

SKU

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.

Software

LabView

NAME

National Instruments

DEVELOPER

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.

Data plotting

3



Software

QGIS

NAME

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.