Using Laser Induced Breakdown Spectroscopy (LIBS) to investigate Prehistoric eating habits in Saudi Arabia

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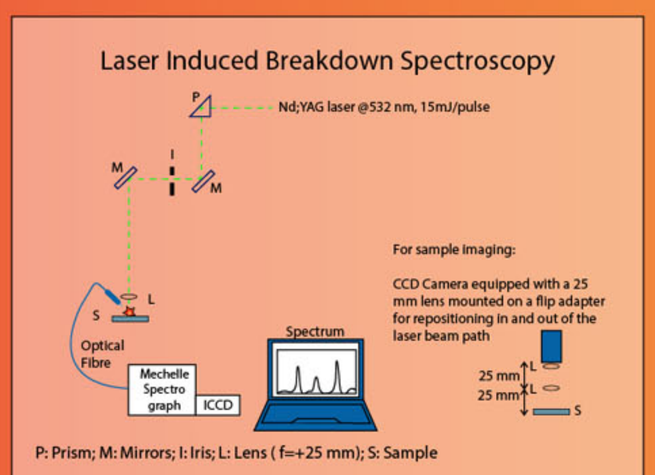
Reconstructing Temperatures through Elements



P: Prism; M: Mirrors; I: Iris; L: Lens (f=+25 mm); S: Sample

Figure 1: A 532 nm Nd:YAG laser beam of ~ 15 mJ energy is focused on the shell on a ~ 90 µm diameter area. The plasma, created by the interaction of the laser beam with the sample, emits light which is collected by an optical fiber and analyzed into different wavelengths by a high resolution($\Delta\lambda$=0.1 nm) Mechelle spectrograph, which is coupled with an ICCD camera. Temporally resolved spectra are recorded at 500 ns after the laser pulse for 2 microseconds. A series of 3 spectra is recorded for every sample location, each spectrum being an accumulation of 5 single-shot spectra.

LIBS is able to rapidly analyse the elemental composition of materials. It is based on the atomic emission spectroscopy of plasma, generated by focusing a high intensity laser beam onto the material and provides qualitative and quantitative results by monitoring the intensities of the material's chemical constituents (**fig. 1**).

Herein, we present the spectral analysis of carbonate from different growth lines of a *Strombus fasciatus* (Born 1778) shell (**fig. 2,3**). During their lifetime, molluscs record the chemical composition of certain parts of their environment and deposit them into their shell. This is why marine gastropods can be a very good proxy for seasonal temperature change (**fig. 4,5**).

The aragonitic shell carbonate of *S. fasciatus* has different ratios of magnesium and calcium depending on the temperature of the surrounding water.

By measuring the change of the Mg/Ca intensity ratio, which is proportional to the Mg/Ca concentration ratio we can reconstruct the change in temperature and consequently the time of the year when the shell was collected and eaten.

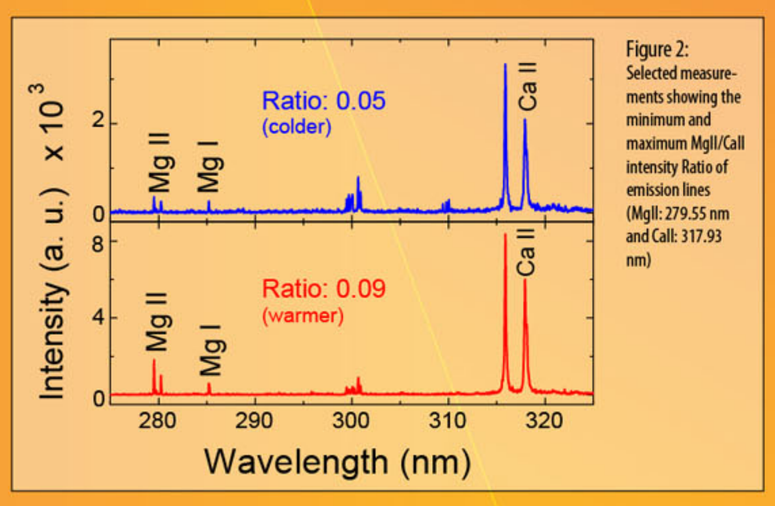


Figure 2: Selected measurements showing the minimum and maximum MgII/CaII intensity Ratio of emission lines (MgII: 279.55 nm and CaII: 317.93 nm)

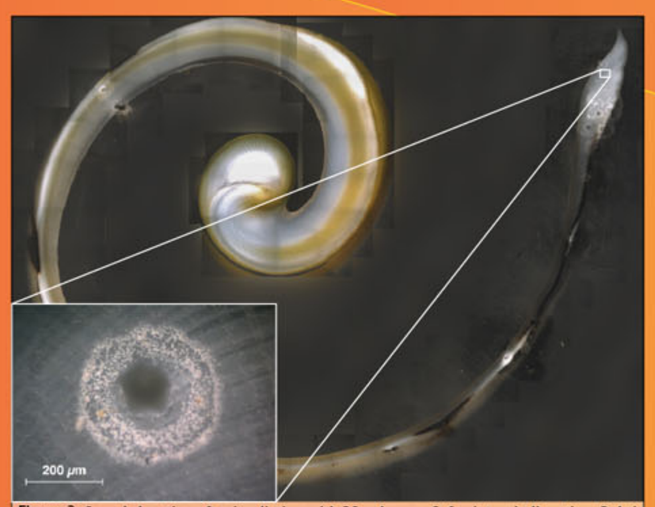


Figure 3: Sample location after irradiation with 30 pulses on *S. fasciatus* shell section. Debris can be found in a circle around the crater and builds up with every pulse.

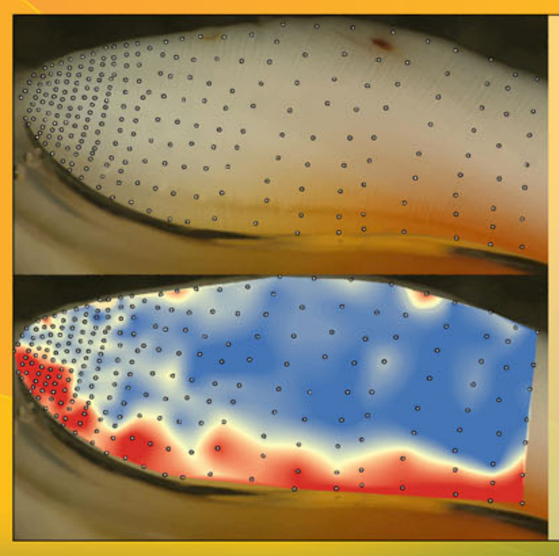


Figure 4:

Shell edge of *S. fasciatus* shell collected in May 2013. Black circles indicate the location of 247 measurements.

Figure 5:

Mapped Mg/Ca intensity ratios on shell edge shows the increase of temperature from winter to early summer. Red colour indicates higher temperature, blue colour indicates lower temperature.

Saudi-Arabian Shell Mounds

Figure 6: View of Farasan shell middens along palaeoshoreline.

The Farasan Islands have the highest concentration of shell middens in the world (**fig. 6**). With over 3000 individual sites, it has been a place of intensive coastal exploitation over a long period (**fig. 7**). By reconstructing the temperature that shells of distinct layers were collected in, we can estimate the time of the year when people occupied the shell mound and analyse the patterns that led to their construction (**fig. 8,9**).

In comparison to other analyses LIBS has many advantages.

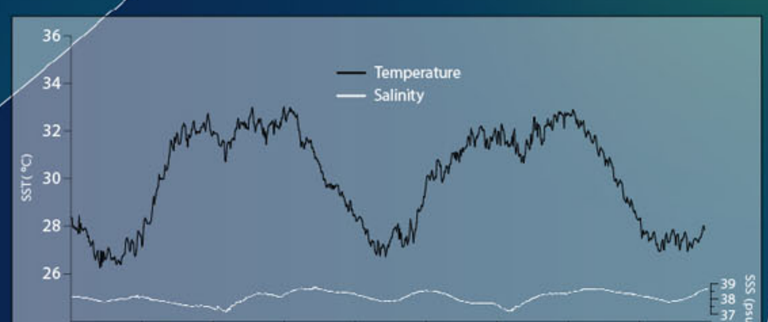


Figure 8: Temperature and salinity change on the Farasan island archipelago over a 2 year period as measured by the NOAA.

Figure 7: Map of the Farasan Island archipelago in the southern Red Sea of Saudi Arabia. Black circles represent the location of registered shell middens (n=3000).

LIBS is **faster**:
- Laser pulse duration: 10^{-8} seconds
- instant acquisition of Mg/Ca intensity ratio
- almost no sample preparation
- computer controlled stage creates rasters of the sample areas extremely fast

LIBS works on a **higher resolution**:
- plasma is created in a 90 µm area
- mapping of Mg/Ca intensity ratio

LIBS is **cheaper**:
- no additional costs except use of laser
- high speed analysis decreases costs per sample

Figure 9: Left: Section of shell midden (scale is 10 m) Right: Living *S. fasciatus* shell. Notice protruding foot with barbed, sickle-shaped operculum on its end.

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