Using LIBS to investigate prehistoric eating habits in Saudi Arabia

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Modern day research in climatology and archaeology requires thousands of samples for a conclusive dataset. LIBS has the unique advantage of taking fast, in- situ measurements at low costs. Moreover it allows to easily replicate data to achieve well-founded and statistically valid results. This is why it is key to further develop it as an alternative to other analyses that are more expensive and time consuming to improve sample numbers and quality of research.

The Farasan Islands in the Saudi Arabian Red Sea are the location of over 3000 shell middens, the prehistoric remains from people eating shellfish [Fig. 1A]. When Neolithic people occupied the islands over 5000 years ago, they consumed marine shells on a large scale and slowly built up mounds of food waste, some of them are over 5 m high [1]. To investigate how often and how regular people came to eat shellfish on the islands, we reconstruct the season that the shells died in by using their ability to record the water temperature in the chemical composition of their shell.

Interestingly, the elemental and isotopic composition of the shells is modified along the growth lines as a function of the water temperature variations from summer to winter. We can use the composition of the youngest line to find out at which time of the year the shell died (Fig. 1B). By defining the Season of Death for shells from the whole mound, we can reconstruct how much people ate at different times of the year.

The analysis of shells requires many samples in order to get representative and statistically valid results. This is a problem for many archaeologists because, generally, the study of elemental components is time consuming and very expensive. Often, the results are based on too few samples and are hard to interpret.

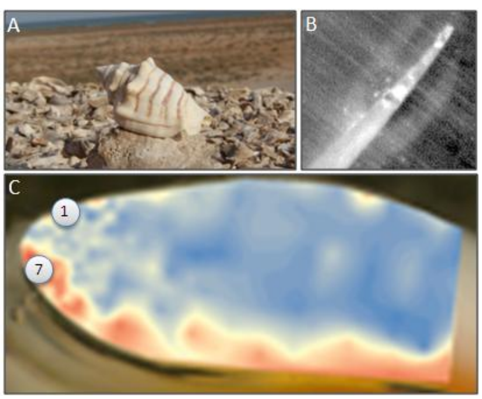

Figure 1: A) *Strombus fasciatus shell on top of shell mound. Modern coastline is visible in the background.* ***B)*** *5 sample locations at the very edge of a juvenile shell.* ***C)*** *Mg/Ca intensity ratios from 250 measurements on the edge of an adult Strombus f. shell. High and low ratios are shown in red and blue respectively. The elemental change correlates with the temperature change from Winter to early Summer.*

On the other hand, Laser Induced Breakdown Spectroscopy (LIBS) is a straightforward technique for rapid analysis of the chemical composition of a huge variety of materials. It is based on the atomic emission spectroscopy of plasma, generated by focusing a high intensity laser beam onto the material. The plasma emission is collected and is spectrally resolved, thus, providing qualitative and quantitative results by monitoring the emission line intensities of the chemical constituents of the material.

The method presents important advantages over conventional analytical techniques, such as the ability to perform *in situ* measurements and without any sample preparation, nearly instantaneous measurement time and easy-to-use equipment of low-maintenance cost. Therefore, LIBS appears to be the most promising technique for the rapid analysis of the vast number of shell middens.

Herein, we present preliminary results of the variation of the Mg/Ca intensity ratio in the plasma (i.e. Mg and Ca ion peaks at 279.55 nm and 317.93 nm respectively) originated from shells, which are composed of aragonitic carbonate. The Mg/Ca intensity ratio in the plasma is proportional to the Mg/Ca concentration ratio [2], which is directly related to the temperature change in the water [3]. Spectral analysis of the samples from different growth lines in the shell showed that tracing the seasonal temperature change is possible [Fig. 1C and Fig. 2] without spending time and/or money on intensive sample preparation or processing.

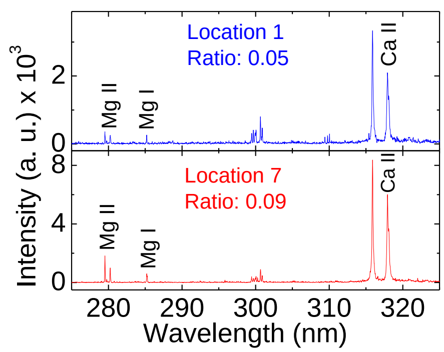

Figure 2: *LIBS spectra obtained upon irradiation of locations 1 and 7 as indicated in Fig 1C. They are the average of 10 single-shot spectra acquired upon irradiation with 10 successive laser pulses at 100 J/cm^2 (Nd:YAG laser; λ=532nm; τ_{pulse}~10 ns). (Emission lines: Mg: 279.55, 280.27, 285.21 nm; Ca: 315.89, 317.93, 318.13 nm).*

However, our measurements suffer from a high relative standard deviation in the range of almost 25-40%. Therefore, optimization of the experimental parameters is necessary, as well as thorough investigation of all Ca and Mg emission lines detected, in order to improve the precision and the reproducibility of the method. Future plans include the implementation of a motorized translation stage for faster sample acquisition with the purpose to automatically analyze multiple areas on the shell with a preset sampling pattern. This way it will be possible to analyse the gigantic amounts of data kept within the shell mounds.

Acknowledgements

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