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Original Research Article

Analysis of spatial distribution of elements in the coral plasma using space resolved spectroscopy

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ABSTRACT

Chemical composition of corals is important information to classify them. Study of laser induced plasma is an effective tool to understand the composition of corals. In the present study, we have investigated the laser induced breakdown spectra of various coral samples for elemental composition. Also the spatial variation of different plasma species in the coral plasma was examined. The elemental compositions of corals are a good record of ecological history. The presence and variations of different elements in the corals indicates alteration of the parameters of environment including hotness/coldness of sea water, salinity, winds, pollutants and major cyclones. The fluorescence in corals is closely related to river runoffs. The presence of rare earths in corals indicates the change in surrounding seawater composition. Our studies indicate the presence of some of the ecologically important elements in the samples. Also, fluorescence is detected in some specimens. The variations in the laser induced breakdown spectra (LIBS) for different input laser fluence are studied for optimizing the ablation conditions. The spatial distribution of elements in the coral plasma was analyzed using space resolved spectroscopic analysis.

1. Introduction

Corals may be regarded as plants which have advantageous green growth (zooxanthellae) inside their tissues. They construct an aragonite skeleton (calcium carbonate) wherein minor components may be consolidated, either by different cycles (such as liquid considerations, inclusion in particular positions in the lattice structure of crystal, adsorption, and so on) or by replacement of Ca^{2+} for divalent ions [1, 2]. Corals have the capability of utilizing intermediately recorders of marine conditions. The consolidation of few synthetic tracers inside the skeleton is broadly reported. Corals give a persistent time-domain recording of marine climate and have been utilized to screen past sea water temperature via either isotopic (O^{18}) or chemical (Mg/Ca, Sr/Ca, B/Ca) records safeguarded inside the aragonite skeletal cross-section [3]. Corals offer a rich document of past environment changeability in tropical sea regimes where device measured information are restricted and where or insight into multi-decadal environment responsiveness is deficient [4]. During the last 10 years, there has been a deliberate work to distinguish new climate tracers in corals and foster more modern methods for information extraction and estimation [5, 6]. Among these, Laser-induced breakdown spectroscopy (LIBS) has been proved an emerging effective strategy for coral examinations.

LIBS is fast field-prepared scientific procedure that gives prompt and negligibly horrendous examinations of gases, liquids and solids. In the LIBS technology, an intense pulsed coherent electromagnetic (laser) radiation is centered on to the chosen coral sample to generate the plasma or laser flash. The

emissions from the ions/ atoms in the generated plasma is gathered on the focal point by using a lens or an optical fiber and observed with the help of a spectrometer. The emission spectrum may be utilized in the determination of element's composition of the coral sample as well as the element's density of the coral sample. The incredible allure of LIBS is that negligibly small or no preparation of the sample is needed to acquire helpful outcomes and the procedure is promptly convenient to the field. LIBS spectra may be aligned to decide specific components of importance.

Another important light based tool to study corals is their fluorescence. The fluorescence is attributed to photosynthetic algal symbionts (i.e. zooxanthellae) and chromophoric fluorescent proteins (FP) in reef-building coral tissue [7]. Coral fluorescence has many potential uses. It is possible to locate cryptically settled coral recruits in the field based on the fact that many will fluoresce brightly when illuminated with blue light. It is also possible to discriminate between members of certain groups of closely related species using fluorescent patterns. Several researchers have attempted to use fluorescence as an indicator of coral and coral reef health. It has also been used as a tracer of freshwater inputs into near shore environments.

The coral species used in the present study are from Lakshadweep Coral Reefs situated in tropical ocean region. The LIBS is used for elemental analysis and to find the spatial electron density distribution of coral plasma. The fluorescence studies are done at different excitation wavelengths to identify the characteristic proteins responsible for the fluorescence.



2. Experimental arrangement and diagnostics

The 1.06 micrometer (10 Hz repetition rate, 9 nanosecond pulse width) radiation from the laser was used for plasma production. The pulses were directed to the target by using a 1.06 micrometer reflecting mirror (50% reflectivity). A lens of quartz having a focal-length equal to 50 cm was used to focus the pulses in to the coral target kept inside the vacuum chamber. The spot size on the target surface was $\sim 0.000396 \text{ cm}^2$. Using a rotary backed diffusion pump the pressure inside the chamber was kept $\sim 10^{-5}$ milli bar during the experiment. The pulses were allowed to fall normal to the target surface. The bulk coral sample was cut and polished in the form of discs (3.5cm diameter, 1cm thickness) and mounted on a motorized target rotator. The objective was turned about an axis in the direction of laser beam propagation to stay away from non-uniform pitting and warming of the target surface. Ablation was done without any surface treatment of the coral sample.

The emission spectra of coral plasma were estimated by noticing the plasma plume symmetrically to the target surface. An optical imaging framework consisting of two converging lenses each of focal length equal to 18 cm was utilized to deliver a 1:1 picture of plume on the entry slit of the spectrograph (Princeton instruments, Spectra Pro – 500i) having a resolution of 0.05 nm. The optical framework was interpreted along the elongation axis of coral plasma utilizing the micrometer driven stage for spatially resolved investigations of the plasma plume. The leave port of the spectrograph was connected to a CCD sensor (Princeton instruments, spec -10). The time integrated spectra from the CCD was acquired by software (Winspec). The fluorescence analysis was done by using Fluorescence spectro-photograph (Varian, Cary Eclipse Fluorescence spectro-photograph).

3. Results and discussion

3.1 Elemental analysis

The most prominent element seen in LIBS spectra is that of calcium. Calcium in corals comes from the skeletal remains of the coral Polyps. A number of emission lines of CI, CII and CIII species of calcium were able to record in the spectra. NIST atomic spectroscopic database was used as reference for elemental identification [7, 8]. All persistent lines of calcium from 350 nm to 900 nm are able to record (Figure 1). Also the intensity of calcium lines is found higher than the other identified species. This may be attributed to the higher concentration of calcium content in corals compared to other elements.

Strontium is an ecologically important element in corals. In coral plasma, Sr/Ca ratio in corals is a powerful tool in reconstructing the hotness/coldness of sea water surface [9]. All the prominent lines of strontium from 350 to 900 nm (Figure 1) can able to record. The intensity of strontium lines in different spectra are found not stable as that of calcium. This may be due to heterogeneous distribution of strontium in different spectra are found not stable as that of calcium. This may be due to heterogeneous distribution of strontium location for Sr is inside the aragonite lattice [10].

Inside the coral's skeleton, the incorporated phosphorus is straightforwardly relative to the encompassing sea water phosphorus concentration and consequently may act as a paleo-oceanographic proxy for verities in sea efficiency and also alterations of home times and wellsprings of deep-water masses [8]. The high productivity of coral reef flats is supported by productive reusing of phosphate inside the framework [9]. Some phosphorus emission lines can able to record in the plasma spectra based on the reference spectra from calcium phosphates (Figure 1).

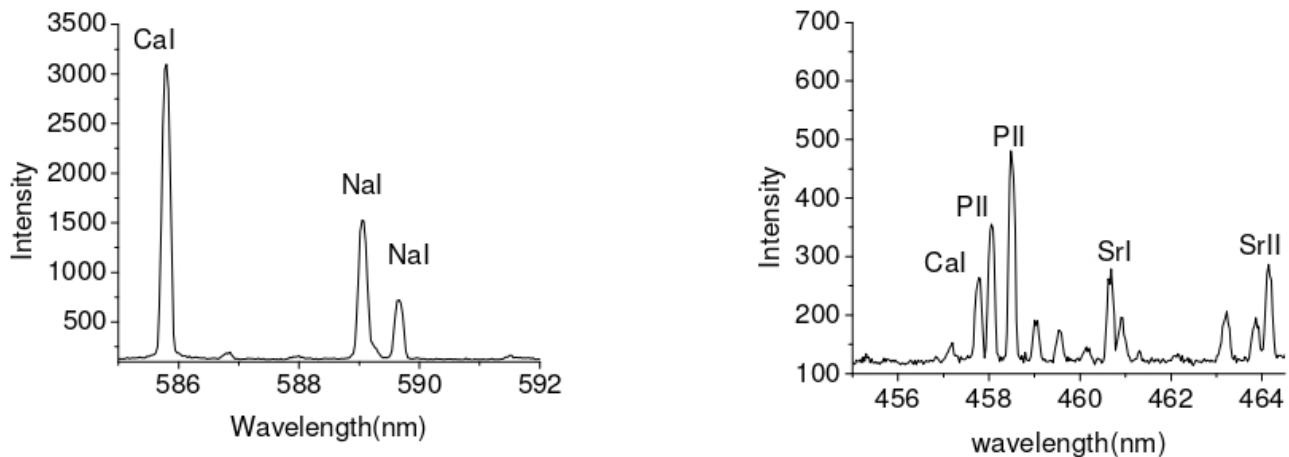


Figure 1. Characteristic emission lines of some elements in the coral spectra.

3.2 Influence of fluence

The characteristics and nature of laser induced plasma unequivocally rely upon laser irradiance. To find an optimum fluence for the LIBS study, spectra were recorded at different pulse energy levels. All other experimental parameters kept constant.

These spectra are recorded at a distance of one millimeter from the target surface at same slit width of 50 micrometer. The fluence varied from 5.05 J/cm^2 to 35.35 J/cm^2 . The intensity of lines found to increase with fluence. There is no marked variations in the number of lines in the spectra. The relative intensity between certain lines found varies with

fluence. The intensity of Ca I (422.67 nm) found smaller than the Sr II (421.55 nm) at higher fluence (Figure 3).

The spectrum was observed at various spatial distances from sample surface up to 20 mm, along the plume expansion direction. Most of the species are found prominent between 2 mm to 4 mm, beyond 4 mm both the intensity and number of species found to decrease. At distances greater than 10 mm the only species found is of calcium.

The Stark spectrum-broadening may be regarded as the advantageous spectroscopic technique in the determination of

electron density of laser plasma. Stark broadened line profile of an isolated atom or singly charged ion may be utilized in determination of electron density [11, 12]. The full width at half maximum of Stark spectrum broadening varies linearly with the electron density. The stark broadened line of CaI species (422.67 nm, $3p^64s^2 - 3p^64s4p$ transition) may be used in the determination of electron density variation in the direction of plume expansion (Figure 4).

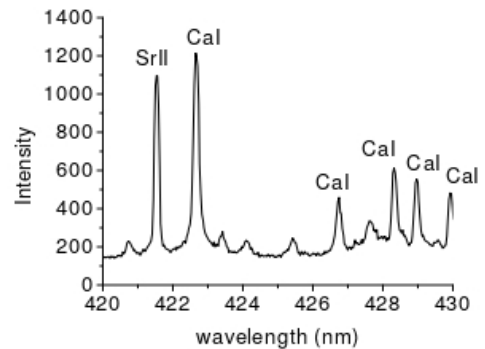
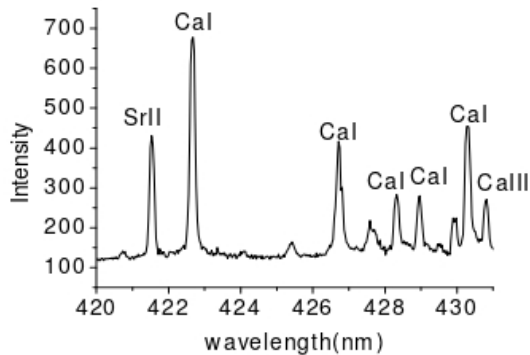


Figure 2. Spatial variation in the spectra.

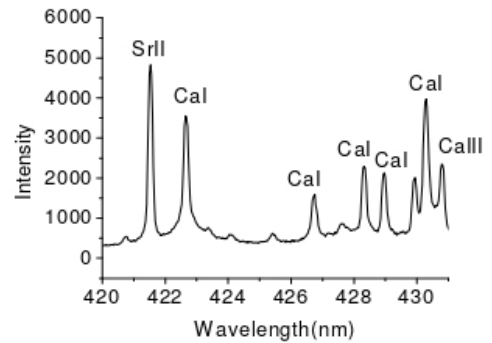
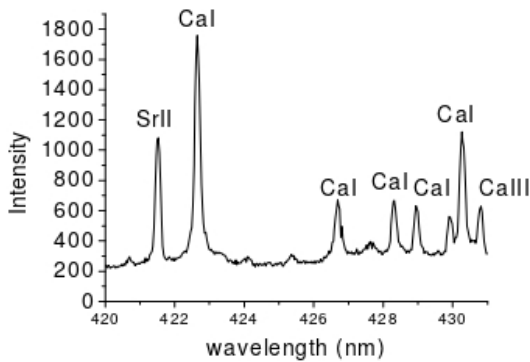


Figure 3. The variation of spectra with respect to fluence. (a) 5.05 J/Cm², (b) 12.62 J/Cm², (c) 25.25 J/Cm² and (d) 35.35 J/Cm².

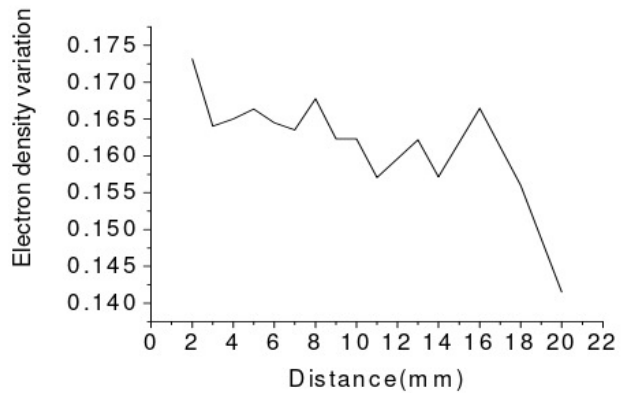
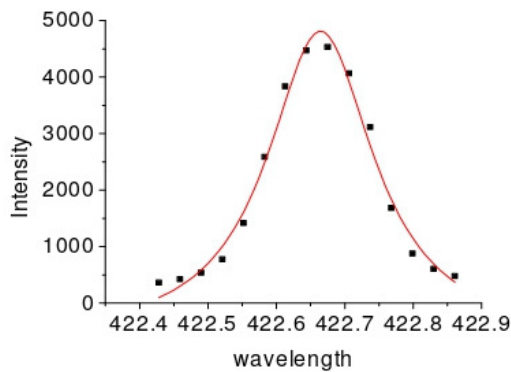


Figure 4. (a) Stark-broadened spectrum of CaI ($3p^64s^2 - 3p^64s4p$) at 422.67 nanometer for 1.06 micro meter laser irradiation at the separation of 2 millimeter from coral-plasma target. (b) Electron density variation of coral-plasma with separation from target surface.

3.3 Fluorescence analysis

The coral-plasma tissues illuminated by sun light contain both the photosynthetic algal symbionts (known as

zooxanthellae) as well as the fluorescent proteins (FP). Both the chlorophyll and FP containing algae have capability of absorbing visible radiation and as a result re-emit the absorbed

radiation as fluorescence at longer wavelengths. The symbiotic algae of reef-building corals are vulnerable under high power illumination typical of shallow tropical coral reefs [13]. The fluorescent proteins absorb light in the UV/blue region and reemit at longer wavelengths in the visible region. The main function of fluorescent proteins is to protect the photosynthetic algal symbionts from harmful UV/blue radiation. The excitation wavelength and corresponding peak emission wavelengths obtained are shown in the Table 1.

Table 1. Observed values of the excitation wavelength and corresponding peak emission wavelengths.

| Excitation (nm) | Emission (nm) |
|-----------------|---------------|
| 290 | 445 |
| 300 | 424 |
| 310 | 421 |
| 320 | 423 |
| 330 | 424 |
| 340 | 426 |
| 350 | 432 |
| 360 | 450 |
| 420 | 490 |

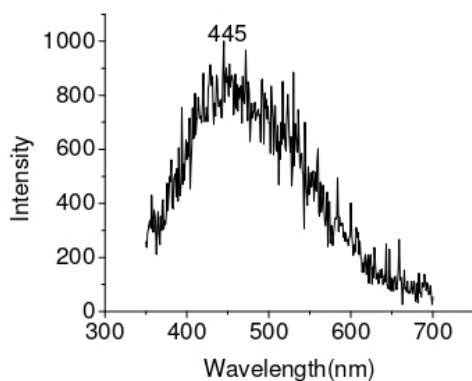


Figure 5: The fluorescence emission spectra of coral excited at 280 nm.

The emissions obtained for the excitations in the UV (280 – 360 nm) and violet 420 nm regions and the respective emission maxima are in 400 to 450 nm and at 490 nm respectively, which approximately matches with the reported broad fluorescence emissions from the GFP (Green Fluorescent Proteins) like proteins [14, 15]. The species emission at 432 nm for the excitation of 350 is stock shifted to 82 nm is well match with the reported P-440 fluorescent protein pigment in the species *Pocillopora damicornis* [13].

4. Conclusions

LIBS spectra provide the details of elemental composition of corals. Due to heterogeneous distribution, trace elements in corals do not give a consistent intensity profile. Higher fluence found affects the relative intensity of lines. Spatial studies show most of the species present from 2 to 4 mm from the

target surface. The fluorescence analysis is useful to identify the fluorescent proteins in corals.

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