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Letter

Gallstone magnesium distributions from optical emission spectroscopy

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Abstract: This work reports measurements of calcified gallstone elemental compositions using laser-induced optical emission spectroscopy. The experimental results support the importance of the magnesium concentration in gallstone growth. Granular stones reveal an increased magnesium concentration at the periphery of the granules, suggesting the inhibition of further growth. Non-granular gallstones reveal lower overall magnesium concentrations but with higher values near the center.

Keywords: laser-induced breakdown spectroscopy; atomic spectroscopy; plasma spectroscopy; laser spectroscopy; physical properties of biomaterials.

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1. Introduction

Cholelithiasis affects the morbidity of adults and increases mortality but it depends on specific population characteristics. For instance, the gallstone disease cases are higher in the north than in the south of India [1]. This work evaluates magnesium concentrations and elemental compositions by collecting spectra during laser ablation of extracted gallstones. Magnesium has many essential roles in fundamental biological functions, and in turn, deficiency provokes several biochemical changes. Sufficient intake is important in maintaining magnesium homeostasis, but average amount of magnesium in today's menu has diminished over the years. Magnesium is an important mineral constituent of various unprocessed diet such as green leafy vegetables, fish and whole grains. Deficiency of magnesium may cause insulin hyper-secretion and dyslipidemia which may facilitate gallstone formation [2–6]. Of interest are calcified non-granular as well as granular gallstones in order to contribute to the understanding of human gallstone progression. However, complimentary in-situ diagnoses may further elucidate the role of magnesium in gallstone growth.

2. Results

Figure 1 illustrates typical gallstone appearances and cross sections. The cross-sectional view of the granular stone (Fig. 1 (b)) indicates different granules of different diameters. In this work, it is of particular interest to analyze and quantify granules with different diameters.

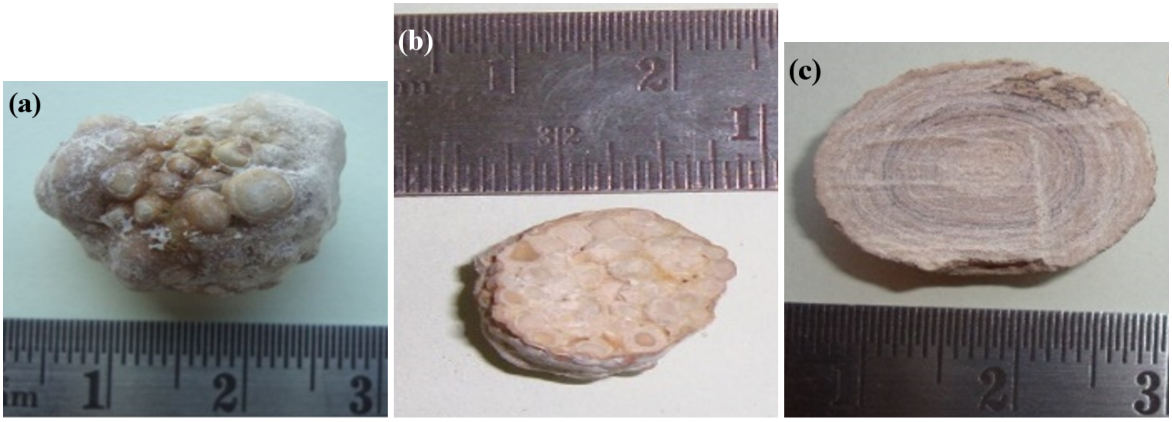

Figure 1. Calcified gallstones: (a) Granular gallstone, and cross-section of (b) granular and (c) non-granular stones.

In the experiments, the samples are mounted on a translation stage and are moved during the measurements. The spectra are collected from different points along the gallstone diameter. The identified spectral lines are due to calcium (Ca), magnesium (Mg), phosphorous (P), iron (Fe), sodium (Na), and potassium (K). The neutral spectral lines of the lighter elements like carbon (C) at 247.8 nm and 229.6 nm, hydrogen (H) at 656.3 nm and oxygen (O) at 777.4 nm have also been identified in the recorded spectra. The simultaneous detection of the lighter elements C, H and O is advantageous in the gallstone experiments. Generating laser-induced breakdown allows one to record and quantify occurrence of lighter elements, which in turn confirms that optical emission spectroscopy is preferred over other conventional analytical techniques such as inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Figure 2 illustrates typical recorded spectra from granular gallstone in the wavelength range of 200 to 500 nm. The spectral line positions of the indicated elements have been identified and compared with the National Institute of Standards and Technology (NIST) data base [7]. Clearly, the magnesium concentration is higher at the periphery than at center.

The spectral line intensity is proportional to concentration of the species. For a particular species transition in the samples, the intensity will directly reflect concentration if other parameters such as temperature do not to vary significantly. In the experimental runs, the average plasma temperature is within $\pm$ 10% as measured using standard Boltzmann plot methods. The recorded spectra of non-granular gallstone (not shown) indicate presence of the same spectral lines. However, the spectral features show differences in the intensities of the Mg I 280.2 nm line and the Ca I 393.0 nm when comparing center and periphery data. Calcified, non-granular gallstones show concentrations of Mg, Ca, Na, P and K that are higher in the center than in the periphery. The relative intensities of the spectral line of Mg I at 280.2 nm were recorded by focusing the laser beam at five equidistant points across the gallstone to evaluate the variation of the Mg concentration. Figure 3 illustrates results for non-granular gallstones in agreement with reported data [8,9], and Fig. 3 shows the measured variations for typical 2-mm to 3-mm granules investigated in this work

A gallstone continues to grow for Mg concentrations with a decreasing trend starting from the center or nucleation point. In turn, for Mg concentrations with an increasing trend starting from nucleation point, one may infer that gallstone growth is inhibited and causes the formation of small granules. Our experimental observations agree with work reported in the literature [10].

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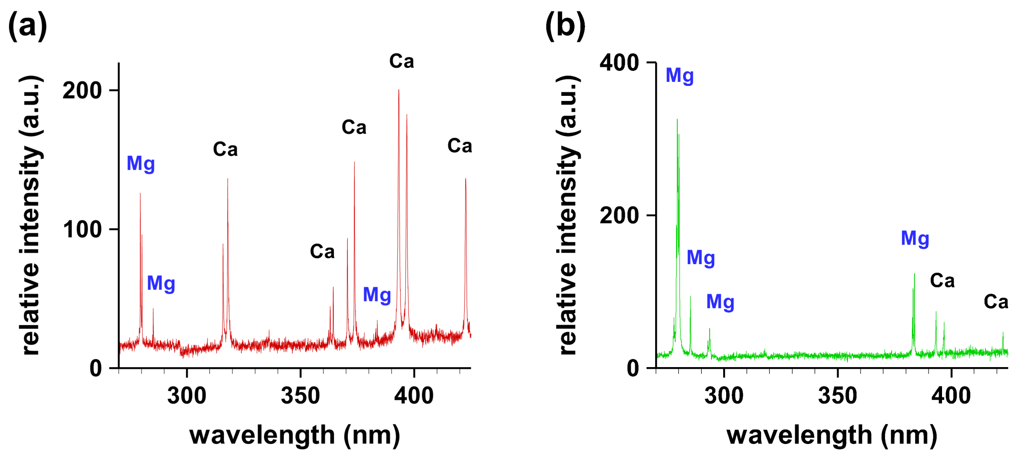

Figure 2. Typical recorded spectral signatures from granules of granular gallstone in the range of 270 nm to 450 nm. (a) Center, (b) periphery.

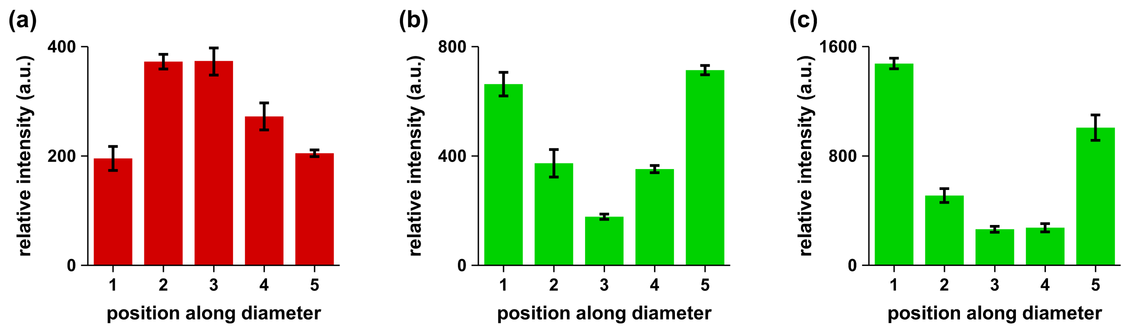

Figure 3. Trends of the measured signals of Mg I 280.2 nm along cross sections. (a) 20 mm non-granular gallstone, (b) 2 mm, and (c) 3 mm granules of granular gallstone.

A higher consumption of magnesium is associated with a reduced risk of gallstone disease with a dose–response relationship that is not accounted for by other potential risk factors including other measured dietary variables. The inverse association was also consistently present in the subgroups of potentially confounding variables which suggest protective effects of magnesium consumption against cholelithiasis.

3. Conclusions

The spatial variations of magnesium concentrations in different granules have been investigated by measuring the Mg I 280.2 nm line at various points in calcified gallstones. The formation mechanism of granular gallstone is different from non-granular gallstone samples obtained from same geographical region. The presented experimental results reveal that Mg is an important mineral, which inhibits or allows further growth of gallstone depending upon its concentration change from the point of gallstone nucleation.

4. Materials and Methods

The experimental arrangement includes a Nd:YAG laser device and a spectrometer equipped with an intensified charge coupled device. Previous work [11,12] describes further details of the experimental setup. Laser pulses of 20 mJ at a repetition rate are used to record data with acceptable signal-to-background and signal-to-noise ratios. Laser-induced breakdown spectra of the gallstone samples show a spectral resolution of 0.1 nm and 0.75 nm in the spectral range of 200 − 500 nm and

$200 - 900$ nm, respectively. The gallstone samples are from the Assam medical college, Dibrugarh, Assam, in the north-east region of India, and were shipped to the laboratory in Allahabad, Uttar Pradesh, in sealed pots for the spectroscopy studies.

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Author Contributions: The individual contributions of the authors include: AKP, NKR, RK, and AKR conceived, designed, performed the experiments and drafted the initial version of this paper; PKR contributed medical insight; CGP collaborated on various aspects of this work, edited the initial draft, and prepared the manuscript for MDPI submission.

Conflicts of Interest: The authors declare no conflict of interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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