

Evaluation of laser-induced breakdown spectroscopy (LIBS) as a new *in situ* chemical sensing technique for the deep ocean

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Abstract—Present day expeditionary oceanography based on short term ship and submersible deployments is beginning to shift to an ocean observatory mode where long term temporally focused studies become feasible. As a result, a greater need for *in situ* chemical and biological sensors is evolving. Laser-induced breakdown spectroscopy (LIBS) possesses many of the characteristics required for such *in situ* chemical sensing, and is a promising technique for field measurements in extreme environments. LIBS has many possible applications in the ocean, including the analysis of rocks, sediments, and hydrothermal vent fluids. Although many LIBS researchers have focused their work on solids, very little attention has been paid to bulk liquid analysis, and especially on the effect of oceanic pressures on LIBS signals. In this work, preliminary laboratory experiments are presented to validate the technique in a simulated deep ocean environment; more specifically, the focus is on using LIBS to study hydrothermal vent fluids.

I. INTRODUCTION

Present day oceanographers primarily use AUVs, ROVs, and submersibles in tandem with ships for expeditionary-oriented research. Time limitations due to factors such as human endurance and operational costs require most studies to be irregular and short term. In addition, few sensors exist for *in situ* chemical analysis; as a result, water and fluid samples are often collected and analyzed shipboard or in a land-based laboratory. Such analysis can lead to alterations of the fluid chemistry due to pressure and temperature change that often results in the irreversible precipitation of analytes. Additional difficulties exist for studying the chemistry of hydrothermal vent fluids due to the corrosive nature of the environment, the high temperature of the fluid, and contamination from entrained sea water. As oceanography enters a new mode of long term studies using ocean observatories, an increased need for *in situ* sensors has developed. New sensors take a considerable time to design, develop, and validate; thus, we must begin to evaluate emerging analytical techniques and determine if they are viable for *in situ* measurements in the ocean.

Laser induced breakdown spectroscopy (LIBS) is a promising analytical chemistry technique for field measurements in

extreme environments, such as the deep sea, and possesses many of the characteristics required for *in situ* chemical sensing. LIBS is a type of atomic emission spectroscopy that utilizes a high power pulsed laser (Nd:YAG laser, 1064 nm fundamental wavelength with <10 ns pulses). The laser is focused onto a sample with a series of lenses to create a high temperature plasma by ablating a small amount of the solid, liquid or gas specimen. The resulting ionic and atomic line emission is characteristic of the composition. The emitted light is focused using a series of lenses on to an optical fiber that delivers it to a spectrometer capable of resolving the emitted lines. The measured spectral lines can be compared with databases of known wavelengths for element identification.

LIBS has myriad possible applications in oceanography. For example, LIBS could be used for the analysis of deep sea sediments, rocks, shells, and ocean fluids, including hydrothermal vent fluids. One of the greatest advantages of LIBS is its capability to simultaneously detect multiple analytes, which is critical for understanding the chemistry of deep ocean environments. LIBS does not require consumable reagents or sample preparation. LIBS allows stand-off measurements to be collected, making it suitable for high temperature use in corrosive environments. LIBS does not significantly perturb the specimen, and is relatively, non-destructive and non-invasive, requiring a minimal sample (picograms to nanograms). In addition, rapid and repetitive measurements are possible.

LIBS has potential applications in many ocean environments. However, as a proof of concept, we have focused our work on one extreme ocean environment, mid-ocean ridge hydrothermal vents. Vents are the result of seawater circulating through the permeable oceanic crust, so that hot fluids exit at discrete high-temperature vents (200-405°C at ambient pressures of 1.5×10^7 to 3.7×10^7 Pa (150 to 370 bar)), while low-temperature (usually < 35°C) fluids seep from porous surfaces [1]. Fluid chemistry is altered due to interaction with the host rock, phase separation into a mixed liquid-vapor form, and possibly magma degassing. Some alkalis (e.g., Li, Na, and Ca) and transition metals (e.g., Fe, Mn, Cu, and Zn) are leached

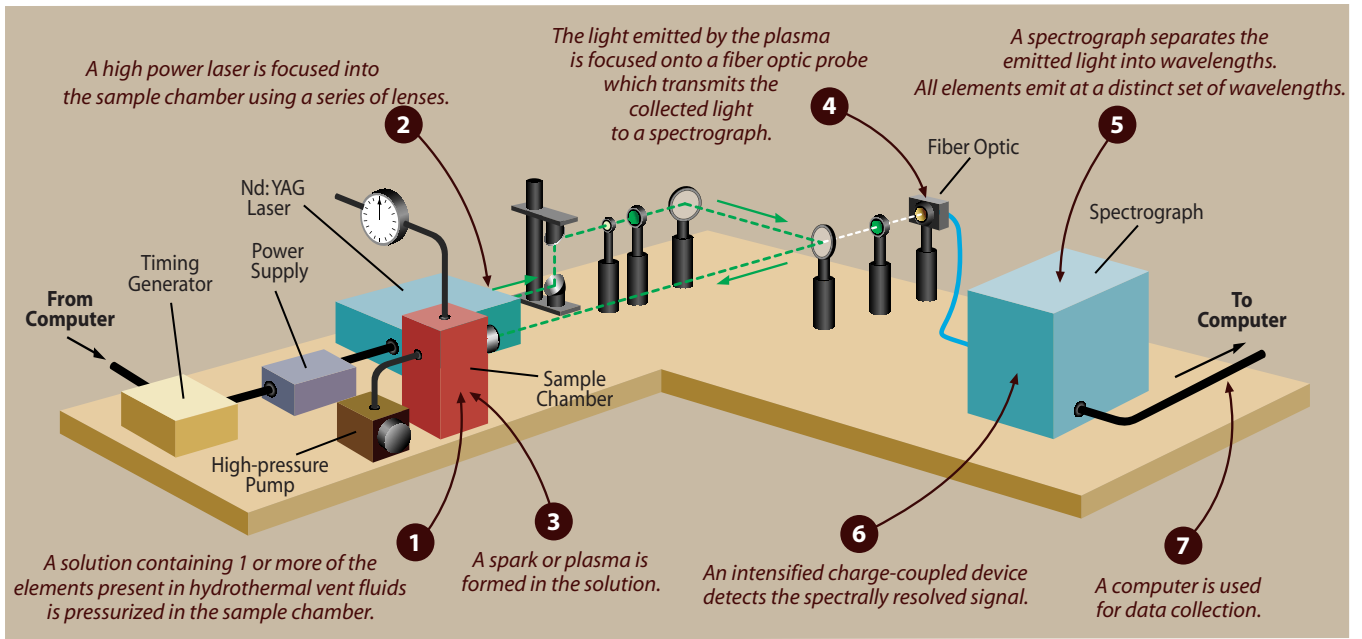


Fig. 1. Experimental Set-up

from the host rock into the hydrothermal fluid. Other analytes, such as SO_4 , precipitate out of the fluids [1]. Reviews of hydrothermal vent fluid chemistry are provided by Von Damm and Butterfield *et al.* [1], [2]. Preliminary results support the feasibility of using LIBS to detect elements important in vent fluids [3], [4].

II. EXPERIMENTAL SET-UP

A laboratory system was designed to detect analytes in a high pressure aqueous environment, as detailed in Figure 1. A Big Sky CFR-200 Nd:YAG laser operated at the fundamental wavelength of 1064 nm with a repetition rate of 5 Hz was used for plasma excitation. The laser is equipped with a motorized variable attenuator, serially controlled by a computer, that allows laser pulse energy to be varied from 0 to 200 mJ, in increments of <1 mJ. A timing box (Berkeley Nucleonics Corporation Model 565) was used to accurately control the firing of the laser in relation to the turn-on of the spectrometer. The important LIBS timing parameters have been described previously [5], [6] and are depicted in Figure 2.

A cubic titanium sample chamber (3.5" x 3.5" x 3.5") was designed to connect with a metering pump (Eldex Model: A-30-S) using Swagelok fittings to pressurize fluid samples up to 4×10^7 Pa (400 bar). Two sapphire windows (Meller Optics - MSW 100/125, 1" diameter x 0.125" thick, AR coated at 1064 nm) both allow laser pulses to enter the cell and the plasma to be observed from the side of the cell (orthogonal to the entering laser beam). AR-coated optics were used to focus the laser beam into the chamber. Additional optics were used for collection of the plasma light onto an optical fiber that delivers it to an Echelle spectrometer (LLA Echelle Spectra Analyzer ESA 3000). The spectrometer is capable of detecting elements

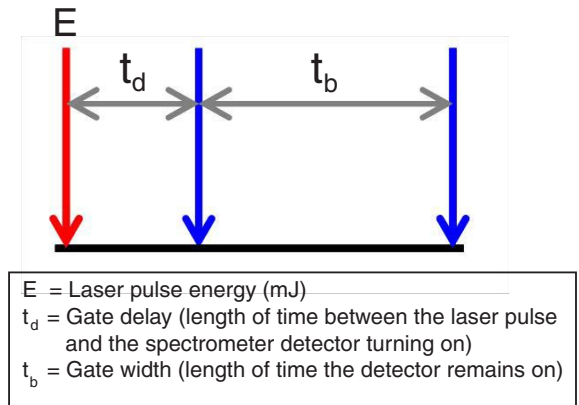


Fig. 2. LIBS Timing Parameters

with wavelengths of 200 - 780 nm with a spectral resolution of 10 to 50 pm.

Solutions were made using de-ionized water, NaCl and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, and all concentrations are listed in parts per million (ppm, wt./vol.).

III. DATA ANALYSIS

The accurate identification of LIBS emission lines is essential for determining the chemical constituents of a sample. A statistics-based data processing scheme was developed to reduce noise in spectra and to average spectra taken under the same conditions. A dark background spectrum is initially subtracted from all raw spectra. Since the resolution of the Echelle spectrometer is greater than the width of the peaks of interest the data are then binned. Shot-to-shot variability was examined, and the formation of a strong intensity plasma

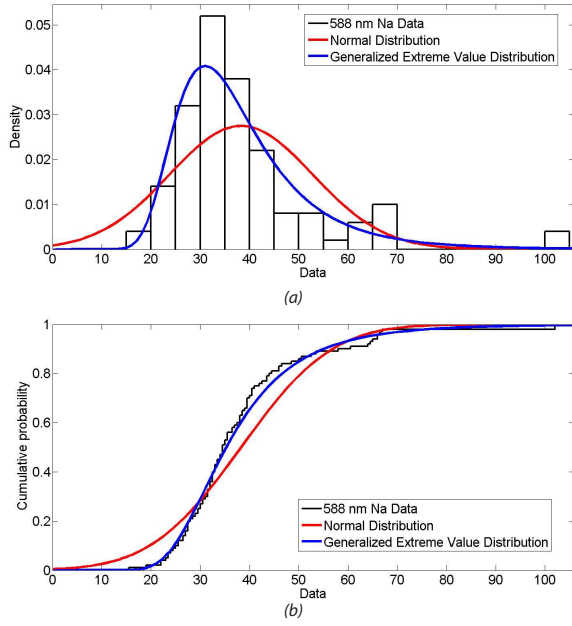


Fig. 3. Na(I) (588.995 nm) single shot data showing they data fit a generalized extreme value distribution (blue) and not a normal distribution (red). (a) Probability density function (PDF) (b) Cumulative density function (CDF)

was, found to be a rare event. The statistical distribution of the data follow a generalized extreme value distribution (GEVD) (Figure 3), and is dramatically non-normal. Because very few intense plasmas are excited, multiple shots can be accumulated on the ccd to create a single spectrum. These spectra were also found to follow a GEVD (Figure 4) due to the fact that intense plasmas are so rare.

As a result of the high plasma variability, when multiple spectra are taken under the same conditions, the raw spectra cannot simply be averaged. Instead, a generalized extreme value maximum likelihood estimator is employed. The GEVD combines three types of extreme value distributions, the Gumbel, Frechet, and Weibull, into a single form. When data are fit to this distribution, the result is the form that best describes the data. The GEVD has the pdf

$$f(x|k, \mu, \sigma) = \left(\frac{1}{\sigma}\right) \exp\left(-\left(1 + k \frac{(x - \mu)}{\sigma}\right)^{-\frac{1}{k}}\right) \star \left(1 + k \frac{(x - \mu)}{\sigma}\right)^{\left(-1 - \frac{1}{k}\right)}$$

for

$$1 + k \frac{(x - \mu)}{\sigma} > 0$$

When $k = 0$, the distribution is Gumbel, when $k > 0$, the distribution is Frechet, and when $k < 0$, the distribution is Weibull. To process the LIBS data, the Matlab function `gevfit`

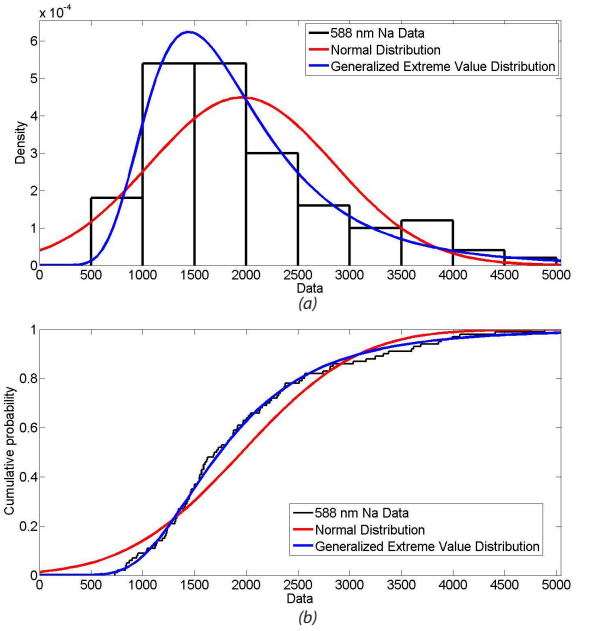


Fig. 4. Na(I) (588.995 nm) for 100 accumulations, showing that the data fit a generalized extreme value distribution (blue) and not a normal distribution (red). (a) Probability density function (PDF) (b) Cumulative density function (CDF)

is used to iteratively determine the maximum likelihood estimates of the shape (k), scale (σ), and location (μ) parameters. The location parameter calculated at each wavelength is then plotted to produce a spectrum. Figure 2(a) shows 5 spectra plotted simultaneously before data processing. Figure 2(b) shows the same data after background subtraction, binning over 10 wavelengths, and using the `gevfit` function in Matlab. This processing scheme was used to reduce all measured spectra. The resulting spectra have a large signal-to-noise ratio and analyte peaks can be identified easily. This work suggest that because the data are not normally distributed, simple arithmetic averaging does not yield a good statistical representation of them. Instead, the maximum likelihood estimator described here should be utilized.

IV. GATE DELAY AND PULSE ENERGY

Several factors, including power consumption and size, constrain the design of ocean sensors. The effect of laser pulse energy on signal intensity for analytes in solution at elevated pressure was investigated with the eventual goal of minimizing power consumption. LIBS operation with a small, low power laser would allow a smaller oceanographic sensor to be designed. In addition, timing parameters must be optimized at pressure to maximize signal-to-noise ratios. In order to determine both the optimal pulse energy and gate delay, two analytes (Na and Mn) were examined over a range of pressures [0 Pa (0 bar), 6.89×10^6 Pa (69 bar), 1.38×10^7 Pa (138 bar), 2.07×10^7 Pa (207 bar), 2.76×10^7 (276 bar)], gate delays (50 ns, 75 ns, 100 ns, 125 ns, 150 ns, 200 ns, 300 ns, 500 ns), and pulse energies (10 mJ, 20 mJ, 30 mJ, 40 mJ, 50 mJ,

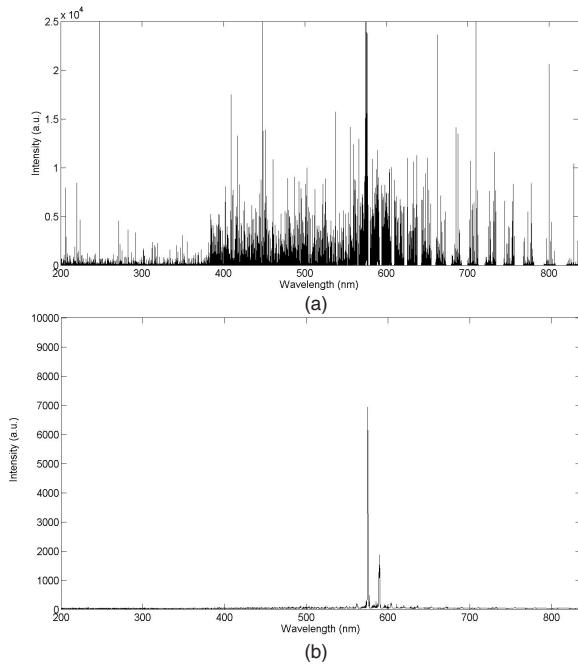


Fig. 5. Spectra of Na(I) (588.995 nm). (a) Plot of 5 raw spectra (b) Processed spectrum (Note: the additional peaks at ~ 575 nm are Ti, thought to be present in the solution due to oxidation of the sample chamber.)

60 mJ, 70 mJ, 80 mJ, 90 mJ, 100 mJ, 110 mJ, 120 mJ, 130 mJ, 140 mJ, 150 mJ, 160 mJ, 170 mJ) to understand their interrelationships. The parameters used for these experiments are 100 on-chip accumulations, $t_b = 200$ ns, amplification = 4000.

The interrelationship of gate delay and energy and how it changes with pressure for Mn(I) (403.08 nm) is shown in Figure 6. These plots indicate that Mn(I) is barely detectable at atmospheric pressure (0 Pa (0 bar)) and only slightly detectable at 6.89×10^6 Pa (69 bar). However, at pressures greater than 6.89×10^6 Pa (69 bar), Mn(I) becomes easily detectable, but only when a small $t_d (< 100$ ns) is used. The data also suggest that a range of energies can be used to detect Mn(I).

Similarly, the interrelationship of gate delay and energy and how it changes with pressure was investigated for Na(I) (588.995 nm), and is detailed in Figure 7. Unlike Mn, Na is detectable at all pressures studied. However, at lower pressures (0 Pa (0 bar) and 6.89×10^6 Pa (69 bar)), the Na intensity is lower than that measured at higher pressures. Again, a short gate delay gives the highest intensity, and a range of energies can be used for Na detection.

In order to simplify the use of LIBS in the deep ocean, the same laser pulse energy and gate delay for the detection of all analytes should be employed. The data presented here illustrate that this can be accomplished for these two elements.

V. CONCLUSION

LIBS is a promising analytical technique that can be used to detect analytes in high pressure, bulk aqueous solutions. A statistically-consistent data processing scheme has been

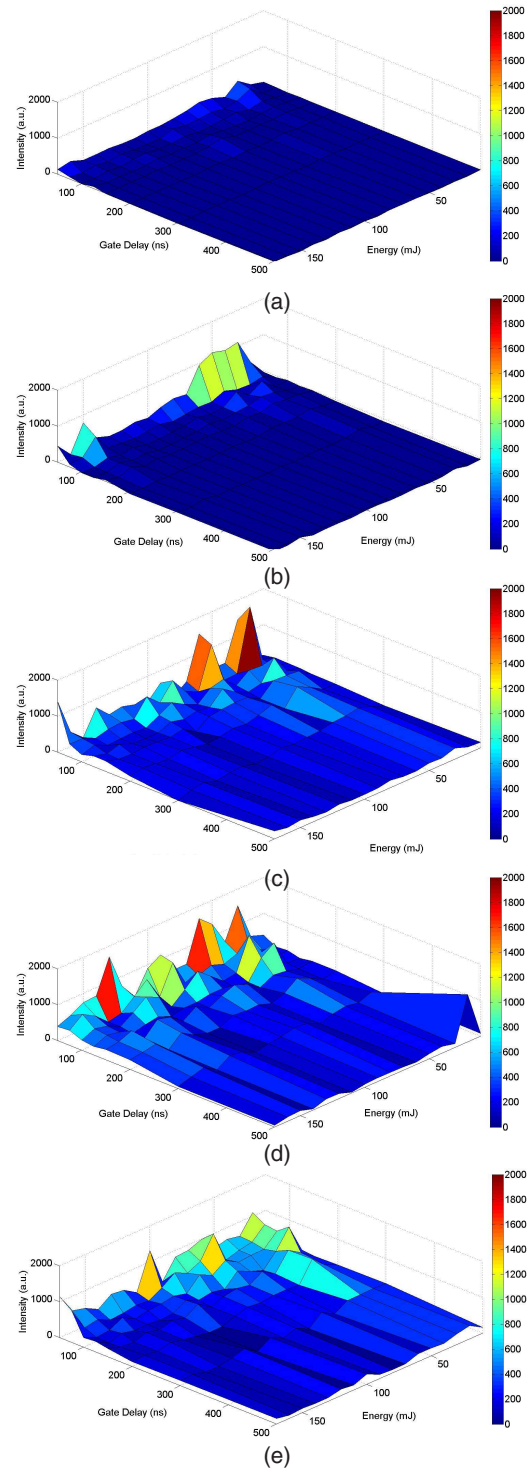


Fig. 6. The interrelationship of pressure, gate delay, and laser pulse energy for Mn(I) (403.08 nm) (a) 0 Pa (0 bar), (b) 6.89×10^6 Pa (69 bar), (c) 1.38×10^7 Pa (138 bar), (d) 2.07×10^7 Pa (207 bar), (e) 2.76×10^7 (276 bar)

presented that allows noisy spectra to be processed into a result where analytes can be identified. When applied to measured spectra of Na and Mn, the results reveal that a short gate delay must be used, although a range of pulse energies is suitable. In addition, some elements, such as Mn, may not be detectable at low pressure, but can be detected at high pressure. Further studies using imaging are needed to elucidate the cause. In addition, future work will determine what other elements are detectable under what conditions in a high pressure aqueous environment.

ACKNOWLEDGMENT

We acknowledge the National Science Foundation for support of this research under grant OCE0352278. Additional support was received from the Deep Ocean Exploration Institute and the Ocean Ventures Fund of the Woods Hole Oceanographic Institution.

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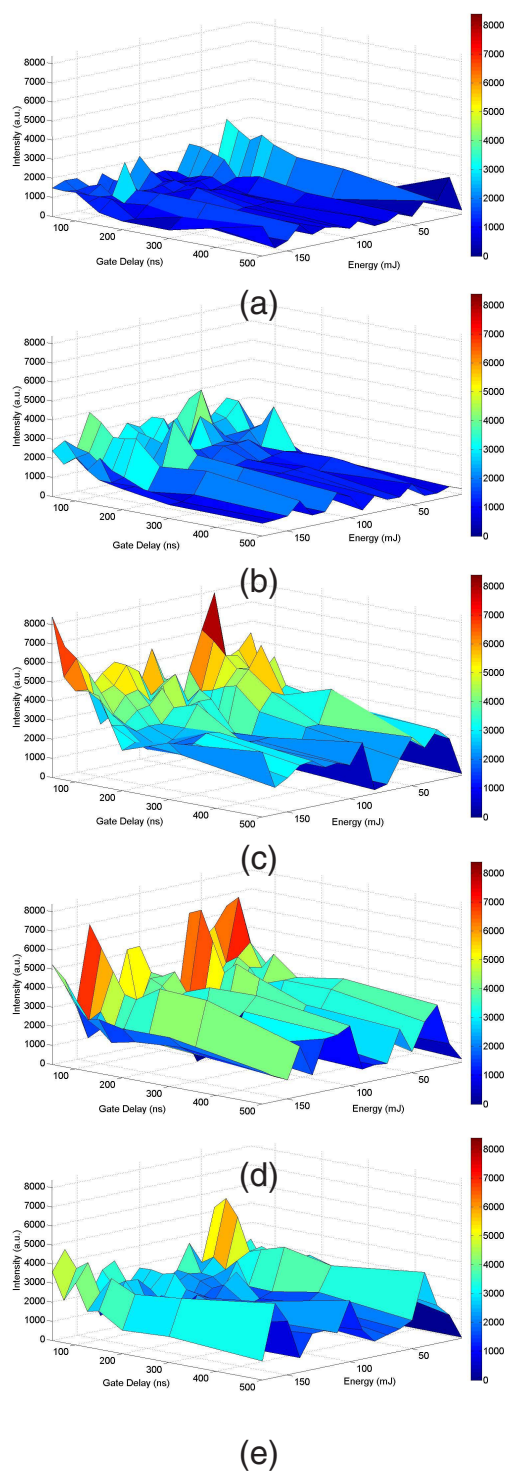


Fig. 7. The interrelationship of pressure, gate delay, and laser pulse energy for Na(I) (588.995 nm) (a) 0 Pa (0 bar), (b) 6.89×10^6 Pa (69 bar), (c) 1.38×10^7 Pa (138 bar), (d) 2.07×10^7 Pa (207 bar), (e) 2.76×10^7 Pa (276 bar)