Investigation of Long-Pulse Laser-Induced Breakdown Spectroscopy for Analysis of the Composition of Rock and Sediment Samples Submerged in Seawater

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***Abstract*—The aim of this paper is to investigate the application of Laser-Induced Breakdown Spectroscopy (LIBS) to qualitatively analyze the composition of various seafloor rock samples in seawater. Well-resolved emission spectra of submerged samples were achieved by using a long laser pulse of duration 250 ns. It was found that the main elements in each rock sample could be successfully identified both in pure water and in seawater. When comparing the measurements made in pure water and in seawater, some effects of the seawater could be seen, however these effects are negligible and do not have any significant detrimental effect on the analytical value of the signal obtained. The results suggest that long-pulse LIBS may be applicable for in situ, multi-element chemical analysis of sediments and rocks in the marine environment.**

Keywords—LIBS; chemical analysis; in situ measurement; laser ablation; marine sediments

I. INTRODUCTION

Deep-sea mineral resources, such as hydrothermal vents, manganese crusts and nodules, are the focus of much attention since they contain various kinds of industrial metals. During mineral surveys on land, in situ chemical analyzers are often used during screening and prospecting of a site because they can obtain data over wide areas at high spatial resolutions. Recently, interest in deep-sea mineral resources has driven the development of a large number of in situ chemical sensors for marine survey. For example, deep sea experiments for detection of Mn^{2+} in seawater using in situ chemical-luminescence sensors have been successfully developed and applied during marine surveys [1]. However, most of the sensors are specialized in chemical analysis of liquids and few in situ sensors have developed for detection of the chemical composition of marine rocks and sediments. Laser Raman spectroscopy, a technique based on inelastic scattering of light, is one of the applicable techniques for in situ analysis of marine sediments, and Breier et al. [2] have recently succeeded in speciation of several kinds of minerals submerged in laboratory environment.

Laser-induced breakdown spectroscopy (LIBS) is also applicable to in situ chemical analysis both of the seawater and of marine sediments. LIBS is a form of atomic emission spectroscopy that analyzes light emitted from atoms and ions of ablated material in a plasma created by focusing a high power pulse laser on a target. Since the atoms and ions of the laser-ablated material emit specific wavelengths of light, elemental analysis of solids immersed in a transparent liquid, such as water or seawater, should be fundamentally possible. Furthermore, LIBS does not require any sample preparation and the results are obtained in real time, making it an attractive option for in situ sensing. In our previous work, we demonstrated that well-resolved emission spectra from solids submerged in water can be observed after irradiation of a low-energy single pulse of ≤ 10 ns duration at pressures up to 30 MPa (300 atm) [3]. A 3,000 m depth rated ocean going LIBS device, I-SEA (In-situ Seafloor Element Analyser) has been developed at the University of Tokyo, and has successfully performed in situ multi-element analysis of fluids and immersed solids during sea trials at a depth of 200 m [4]. This is, to the knowledge of the authors, the first successful demonstration of LIBS in the marine environment. While I-SEA uses a conventional single pulse measurement technique, in Sakka et al. [5] it was demonstrated that significant gains in signal quality could be achieved for metals submerged in water if a long-pulse laser of duration 150 ns is used. Furthermore, the authors reported that increase of hydrostatic pressure up to 30 MPa (300 atm) does not have a significant influence on the quality of the spectrum observed using this technique [6].

Since LIBS is capable of measuring the composition of both solids and liquids, in order to apply LIBS to chemical survey of marine sediments, it is necessary to examine the effect of seawater on signals observed from submerged mineral targets. It has previously been reported that a peak of Na^{+} was detected when long-pulse LIBS measurements were performed on Cu targets in a 5 mM NaCl aqueous solution [7]. Masamura et al. [8] determined that the detection limits of Li, Na, Ca and Mg are 0.1, 1, 10 and 500 ppm respectively when a

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short laser pulse of 8 ns duration is focused directly into bulk aqueous solutions. Considering the concentration of elements in seawater (shown in Table I), it is conceivable that the major elements in seawater may affect the results of LIBS on solid targets.

In order to investigate this point, we perform long-pulse LIBS measurements of the compositions of various rock and sediment samples obtained from the seafloor. First measurements are made with the samples submerged in pure water to obtain the unaffected signals, and identify peaks that can be used to characterize each sample. Next, the same experiments are performed in seawater to examine the effect of seawater on the results. The results demonstrate that while there is some influence of seawater, the effects are small and do not have any significant impact on the analytical value of the signal obtained.

TABLE I. COMPSITION OF SEAWATER [9].

element	Cl^-	Na^+	SO_4^{2-}	Mg^{2+}	Ca^{2+}	K^+
weight %	1.90	1.06	0.265	0.127	0.04	0.038
element	HCO_3^-	Br^-	H_3BO_3	Sr^{2+}	F^-	
weight %	0.014	0.0065	0.0026	0.0013	0.0001	

II. SAMPLES AND EXPERIMENTS

A. Samples

The list of rock and sediment samples used in this work is given in Handbook of Laser-Induced Breakdown Spectroscopy, II. The samples were crushed into powder with a mortar and pressed into pellets in order to make the samples homogeneous. In order to obtain a ground truth, the chemical compositions of the samples have been accurately measured through Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Table III shows the composition of major elements in the samples obtained from ICP-AES analysis. The samples (a) Jade and (b) Hatoma are hydrothermal chimney samples, and are rich in Zn, Pb and Cu. It should be noted the sample (c) Yoron, which is also a chimney sample from the Okinawa trough, does not contain much Zn, Pb and Cu, indicating that this chimney was formed under different conditions from the samples of Jade and Hatoma.

TABLE II. SAMPLE LIST.

Sample name		Type	Location
(a)	Jade	Hydrothermal vent	JADE Site (in the Okinawa Trough)
(b)	Hatoma	Hydrothermal vent	Hatoma Knoll (in the Okinawa Trough)
(c)	Yoron	Hydrothermal vent	Yoron Knoll (in the Okinawa Trough)
(d)	Takuyo	Manganese oxide	#5 Takuyo Seamount (in the Northwest Pacific)
(e)	basalt	Sea sediment	Substrate rock at #5 Takuyo Seamount (in the Northwest Pacific)
(f)	limestone	Sea sediment	Substrate rock at #5 Takuyo Seamount (in the Northwest Pacific)

TABLE III. THE CHEMICAL COMPOSITIONS OF ROCK AND SEDIMENT SAMPLES.

	(a)	(b)	(c)	(d)	(e)	(f)
Ag	0.0182	0.0486	0.0532	0.00151	-	-
Al	0.0114	0.507	0.0357	0.976	6.79	0.251
As	0.0628	0.755	0.855	0.0217	0.00182	0.00106
Ca	0.0173	0.0647	0.114	6.32	9.96	25.2
Cd	0.123	0.0288	0.00492	-	-	-
Co	-	-	-	0.566	0.00760	0.00585
Cu	4.39	5.25	0.105	0.0621	0.0236	0.0113
Fe	10.2	3.50	2.52	9.50	8.66	0.384
Mg	0.0216	0.0478	0.00742	1.03	4.99	0.0890
Mn	0.0766	0.457	0.00503	16.2	0.203	0.473
Ni	-	-	-	0.461	0.0250	0.0272
Pb	12.2	10.3	0.761	0.211	0.0162	0.0042
Sb	0.0215	0.594	0.333	0.00289	-	-
Sr	0.0205	0.313	0.717	0.131	0.0603	0.125
Ti	0.00507	-	-	0.336	1.45	0.0354
Zn	19.8	12.0	0.640	0.104	0.0196	0.0076
***the rest**	53.0	66.1	93.8	64.1	67.8	73.4

*the rest: S, Si, O etc (weight %)

Fig. 1 shows the ideal, theoretically calculated spectra of each sample. The range of wavelengths is set to between 200 nm to 800 nm in accordance with the sensitivity of the detection system that is used for analysis. The intensities of each peak were calculated using the Boltzmann distribution law [10]:

$$I_{ij} = FC^S A_{ij} \frac{g_i e^{-\frac{E_i}{kT}}}{U^S(T)} \quad (1)$$

where I_{ij} is the line intensity of a peak, F is an experimental parameter depending on sensitivity of the observation system at each wavelength, C_s is concentration of emitted species in the sample, k is the Boltzmann constant, $U_s(T)$ is the partition function, A_{ki} is the transition probability, g_k is the statistical weight for the upper level, E_k is the excited level energy, and T is the plasma temperature. The parameters A_{ki}, g_k, E_k and $U_s(T)$ can be obtained from the National Institute of Standards and Technology (NIST) database [11]. The plasma temperature T was set to 8,000 K considering the temperature of underwater plasmas generated on submerged metallic targets during preliminary experiments. From the calculation in Fig. 1, it is noticeable that a higher density of strong lines can be expected at shorter wavelengths compared to longer wavelengths, especially in the spectra of samples from hydrothermal vents.

B. Experimental setup

The experimental setup used is shown in Fig. 2. The laser pulse is generated using a 1064 nm Nd:YAG Q-switched laser, which delivers a single 20 mJ pulse of duration 250 ns-via a

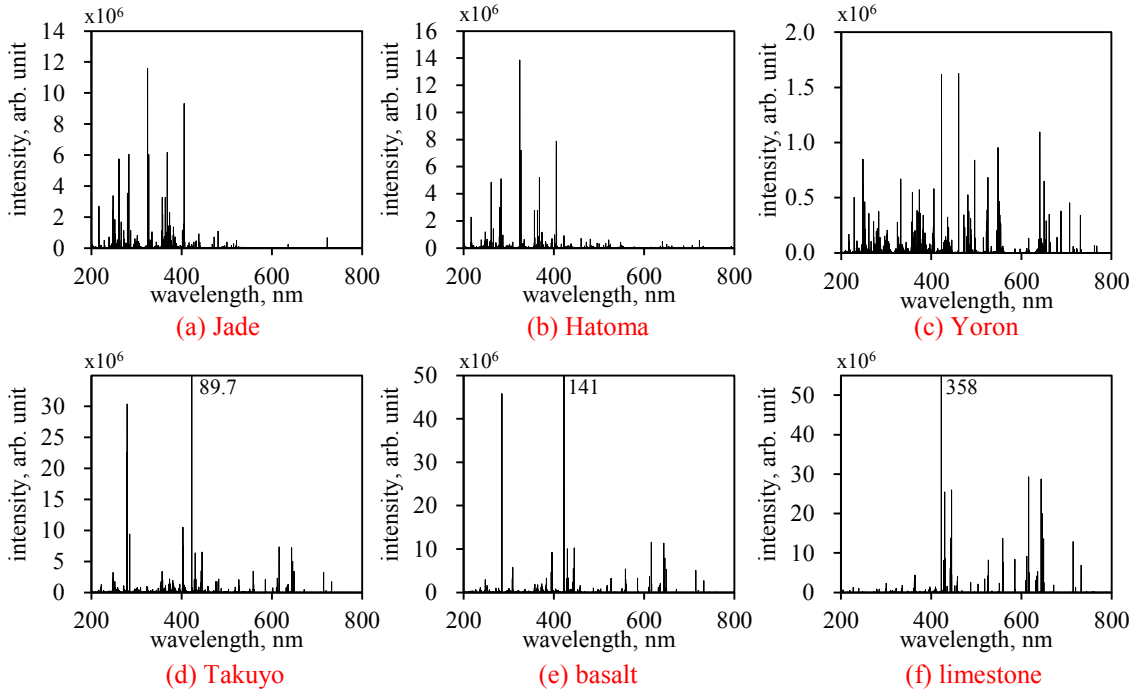

Fig. 1. Calculated spectra of each sample.
(Numbers written beside lines indicate the intensities (x10^6) of the lines)

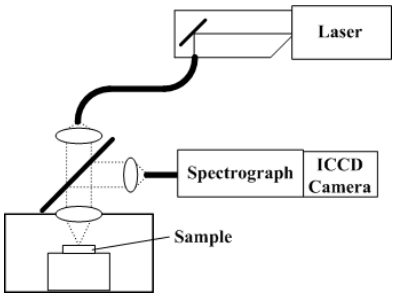

Fig. 2. Experimental setup.

600 µm fused-silica fiber. The laser is focused using a Cassegrain reflecting lens of 5 times magnification. A Cassegrain lens was used since it does not suffer from chromatic aberration. Since the same optical path is used for both delivery of the laser, and observation of the generated plasma, this maximizes the range of observable wavelengths. The laser travels through a pressure window, which is immersed on one side, and is focused onto a target 10 mm away from the face of the lens in water. Spectroscopy was performed by observing the light emitted from the plume through the same optical path used for laser delivery. This allows the plasma to be observed normal to the surface of the target and so maximize the visible cross section. The spectrograph has a focal length of 150 mm with a light throughput of f/4 (Acton Research Spectra Pro 2150). A 600 groove/mm grating and a 50 µm wide entrance slit were used. The spectra were recorded using an intensified charge-coupled device (ICCD, Princeton Instruments PiMAX 1024i) as a detector. The gate width was set to 500 ns, the delay to 500 ns for all measurements presented in this work. The wavelength range of the grating used in this work is limited to a range of 210 nm for each measurement. Considering the richness of information, a lower range of wavelengths is desirable. However, due to the limited sensitivity of detection system below 350 nm, the range was set from 360 nm to 570 nm for the experiments described.

III. Results and Discussion

A. Results in water

The spectra of each rock sample measured in pure water using long-pulse LIBS is shown in Fig. 3. The list of the peaks seen in each spectrum is given in Table IV. The data shown is an average of five spectra and the signals are normalized by the line, which has the strongest intensity in the observed range. The shape of each spectrum differs from each other depending on its composition, and it can be seen that the submerged samples can be identified using long-pulse LIBS. It can be seen that the emission lines of the elements which contain more than 1 % in each sample are clearly visible as peaks in the data. For example, lines of Zn, Cu and Pb can be seen in the spectrum of (a) Jade and (b) Hatoma, which is in accordance with the results of ICP-AES. Spikes of Zn and Pb can also be recognized in the spectrum of (c) Yoron, though in both cases their concentration is less than 1 %. In the spectrum of (d) Takuyo, a significant line of Mn at 403.75 nm can be seen, which cannot be recognized in other spectra. Peaks of Ca are seen in spectra in the samples of (d) Takuyo, (e) basalt and (f) limestone. However, it should be noted that some elements have emission lines that are close together, where the peaks are

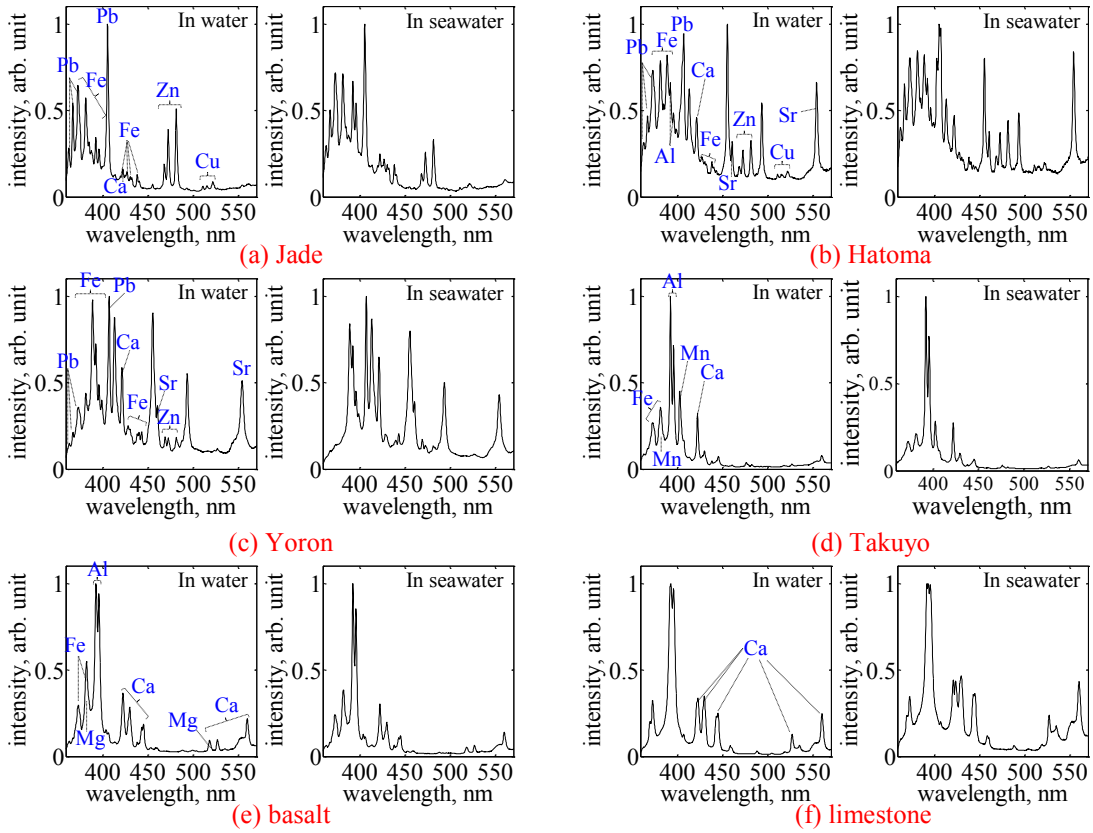

Fig. 3. Spectra obtained using long-pulse LIBS.
(The left spectrum of each sample is obtained in water and the right is in seawater)

TABLE IV. THE CHEMICAL COMPOSITIONS OF ROCK AND SEDIMENT SAMPLES.

element	wavelength [nm]	(a)	(b)	(c)	(d)	(e)	(f)	element	wavelength [nm]	(a)	(b)	(c)	(d)	(e)	(f)
Pb	**363.96**	o	o	o				**Ca**	**430.25**					o	o
Pb	**368.35**	o	o	o				**Fe**	**430.79**	o	o	o			
Fe	**373.49**	o*	o*	o*	o	o		**Fe**	**432.58**	o		o			
Pb	**374.00**	o*	o*	o*				**Fe**	**438.35**	o	o	o			
Mn	**380.67**				o*			**Fe**	**440.48**	o		o			
Fe	**382.04**	o	o	o	o*	o*		**Ca**	**443.50**					o	o
Mn	**382.35**				o*			**Ca**	**445.48**					o	o
Mg	**383.83**					o*		**Sr**	**460.73**		o	o			
Fe	**385.99**	o	o	o				**Zn**	**468.53**	o	o	o			
Fe	**388.63**	o	o	o				**Zn**	**472.22**	o	o	o			
Fe	**393.03**	o		o				**Zn**	**481.05**	o	o	o			
Al	**394.40**		o		o	o		**Cu**	**510.55**	o	o				
Al	**396.15**		o		o	o		**Cu**	**515.32**	o	o				
Fe	**396.93**	o		o				**Mg**	**517.27**					o*	
Mn	**403.75**				o			**Mg**	**518.36**					o*	
Pb	**405.78**	o	o	o				**Ca**	**518.88**					o*	
Fe	**419.91**	o						**Cu**	**521.28**	o	o				
Ca	**422.67**	o	o	o	o	o	o	**Ca**	**527.03**					o	o
Fe	**427.18**	o	o	o				**Sr**	**554.11**		o	o			
								Ca	**558.87**					o	o

*: lines combined into one peak

not resolved, for example, the peaks of Fe I at 373.49 nm and Pb I at 374.00 nm in spectra of (a) Jade, (b) Hatoma and (c) Yoron. This is a particular problem for measurements in water because of broadening of lines that occurs when LIBS is performed in incompressible fluids. However, in most cases, there is still sufficient number of well resolved peaks which can be used for analysis.

B. Results in seawater

Fig. 4 shows the calculated spectrum of seawater. The intensities of each peak were calculated by equation (1). The prominent line in the range between 360 nm and 570 nm, is a peak of Ca at 422.67 nm.

The spectra obtained using long-pulse LIBS in seawater are shown in Fig. 3. Compared to the signals obtained in water, some degradation of peaks could be seen, such as the peaks of Fe I at 373.49 nm and Mn I at 380.67 nm in the spectrum of (c) Yoron, and the peaks of Pb I at 363.96 nm, 368.35 nm and Fe I of 373.49 nm in the spectrum of Takuyo. Nonetheless, most of the peaks in the spectra obtained in water can be seen in those obtained in seawater and it is still possible to distinguish samples by the spectra obtained using long-pulse LIBS in seawater. The line of Ca at 422.67 nm which stems from seawater is hardly seen in the spectra of (a) Jade, (b) Hatoma and (c) Yoron. Considering the samples of (d) Takuyo, (e) basalt and (f) limestone, which are rich in Ca, the spectra of (d) Takuyo and (e) basalt obtained in seawater have almost the same peak height of Ca at 422.67 nm. The fact that the contribution of Ca in water is not seen is partially due to the lower concentrations of elements in liquids, but mainly thought to be due to the fact that atomization of liquid only occurs at much higher energy and power intensities compared to solids during preliminary experiments, and under the condition of the experiments in this work, the breakdown of solids was dominant in the whole process of plasma ablation. In addition, in our experimental setup, the observation system is focused on the light emitted near the center of the plasma, and studies have demonstrated that contribution of dissolved ions is not significant in the center of plasmas generated on solid surfaces [7]. It should be noted, however, that the self-absorption in the peak of Ca at 422.67 nm in the spectrum of (f) limestone in seawater can be seen. Self-absorption occurs when the photons emitted from excited atoms is absorbed by the cooler atoms of the same species in the outer layers. This reduces the observed intensity of the emission line and becomes more evident as the concentration of the atoms in the target sample increases [12]. In this case, Ca^{2+} which stems from seawater might also be atomized by a laser pulse and merged into the outer layer of occurring plasma. Since the sample (f) limestone contains over 25 % Ca, the concentration of the Ca atoms is so high that the light emitted from excited Ca atoms in the target are absorbed by other Ca atoms surrounding the plasma. However, a number of methods for correction of effect of self-absorption on a peak have been established [13, 14] which can be applied when analyzing the signal.

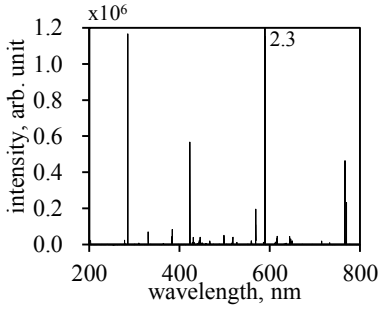

Fig. 4. Calculated spectrum of seawater.

(A number written beside a line indicates the intensity (x10^6) of the line)

It should also be noted that except for (d) Takuyo and (e) basalt, spectra obtained in seawater have stronger background than those obtained in water. A possible explanation of this is that plasma occurs more vigorously in seawater than in pure water. In this case, it may be possible to eliminate the effects of the background by using a longer delay time during the measurements, or by lowering the energy of the pulse used when making measurements in seawater. Future work is necessary to optimize the condition for measurement in seawater.

IV. CONCLUSION

Using long-pulse LIBS, the peaks of the major elements of mineral rock samples could be seen in samples immersed in both water and seawater. From the signals obtained, it is possible to distinguish the samples. Since the samples chosen are representative of the types of rocks found on the seafloor, combined with our previous finding that the long-pulse is not significantly affected by hydrostatic pressure up to 30 MPa [6], the results are expected to have a significant impact for the survey of marine minerals. The effects of seawater were seen in the form of the self-absorption of a line of Ca in a spectrum of limestone in seawater, and increased background signal. Nonetheless, the effects of seawater on spectra are small and there exist various analytical techniques to correct these effects. In our future work, the effect of seawater on how vigorously the plasma occurs will be examined. Furthermore, not only qualitative analysis but also quantitative analysis will be performed on the signals using data processing methods, such as calibration-free LIBS, which does not require drawing calibration curves [10].

To the best of the authors' knowledge, this study is the first to carry out long-pulse LIBS with rock samples in water and in seawater. The results suggest that long-pulse LIBS may allow for in situ, multi-element chemical analysis of sediments and rocks.

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