Analytical Methods to Distinguish the Positive and Negative Spectra of Mineral and Environmental Elements Using Deep Ablation Laser-Induced Breakdown Spectroscopy (LIBS)

Dongyoung Kim¹, Jun-Ho Yang¹, Soojin Choi¹ and Jack J. Yoh¹,*
¹Department of Mechanical and Aerospace Engineering, Seoul National University, 1 Gwanakro, Gwanakgu, Seoul, Korea 151-742

* Corresponding author email: jjyoh@snu.ac.kr
Tel.: +82-2-880-9334; Fax: +82-2-887-2662

Abstract
Environments affect mineral surfaces, and the surface contamination or alteration can provide potential information to understanding their regional environments. However, when investigating mineral surfaces, mineral and environmental elements appear mixed in data. This makes it difficult to determine their atomic compositions independently. In this research, we developed four analytical methods to distinguish mineral and environmental elements into positive and negative spectra based on depth profiling data using laser-induced breakdown spectroscopy (LIBS). The principle of the methods is to utilize how intensity varied with depth for creating a new spectrum. The methods were applied to five mineral samples exposed to four environmental conditions including seawater, crude oil, sulfuric acid, and air as control. The proposed methods are then validated by applying the resultant spectra to principal component analysis (PCA) and data were classified by the environmental conditions and atomic compositions of mineral. By applying the methods, the atomic information of minerals and environmental conditions were successfully inferred in the resultant spectrum.

Keywords: Laser-induced breakdown spectroscopy, LIBS, mineral surface, depth profiling, mineral elements, environmental elements, principal component analysis, PCA.

Introduction
Mineral surface has a record of environmental changes in the area. Minerals also undergo chemical and physical changes on the surface after the long exposure to the ambient conditions. Fine particles moved by liquid or gas flow are also accumulated on the surface. Thus, residues on a mineral surface can be used as an indicator of rich elements of an
environment where minerals have existed. Therefore, surface of minerals can provide potential information to understanding their regional environments. The constituents of a mineral surface can be divided into mineral and environmental elements. The mineral elements are the original substances of the mineral while the environmental elements are formed due to the lifelong exposure to the surrounding. The deeper the depth from the surface of the mineral to the inside, the more environmental influence will disappear while pure substance of the mineral will appear. This is due to accumulation of environmental elements on mineral surface. Mineral surface investigation in space exploration also leads to discovering microorganisms and the presence of water.

Many techniques have been used to analyze minerals, including X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and inductively coupled plasma mass spectroscopy (ICP-MS). Raman spectroscopy is also a useful technique to identify molecules of mineral. Despite the known precision and accuracy of these techniques, sample preparation prior to bringing the samples into a laboratory is one of disadvantages. Furthermore, additional surface depth profiling is not possible via these well-known atomic emission spectroscopy techniques.

Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy used in multi-elemental chemical analysis. A pulsed high-energy laser is focused onto a target material. The high energy density of the surface will generate a plasma in a few nanoseconds. Atoms and ions in the plasma will emit characteristic wavelengths that have information about the atomic composition of the material. By detecting emitted light, it is possible to analyze constituents of the material. Therefore, LIBS technique has been used to analyze matters in various disciplines such as archaeology, geochemistry, space science. In addition, LIBS system can be integrated to a compact and portable instrument for effective use in non-laboratory experiments or field investigations. LIBS has high sensitivity with great ability to detect fine particles. Because LIBS has the ability to ablate the surface of minerals, it is useful for the depth profiling analysis, and thus has been applied in the multi-elemental depth analysis in various fields.

The Mars probe Spirit has discovered mineral coatings on mineral surfaces of Mars different from those of mineral elements. Chemcam measured changes in elements with depth on the surface of minerals by laser shots in Mars. In fact, a high manganese content has been found on the surface of minerals. Chemcam's LIBS data showed that the first one to five shots have different tendencies for shots after those. Shots 1 to 5 are dust or soil of
Mars attached to the surface of minerals. Therefore, it is possible to group similar areas of the environment by elements originating from the surface of the mineral. Degradation mechanisms of materials in cultural heritage has been investigated using LIBS and it is confirmed that systematic decrease of Fe and Mn peak intensities on the surface of the material. Studies on the surface of minerals on Mars have also been done to obtain environmental information. Thus, surveying the surface of minerals is a useful method for obtaining information about unknown environments. However, in a single laser spectrum, it is difficult to analyze data due to a mixture of mineral elements and environmental elements. In addition, since elemental signals change with increasing depths, large amounts of depth profiling data are necessary in order to analyze spectrum changes. However, if mineral and environmental elements are distinguished and presented in a spectrum, they will be analyzed independently from small amounts of data.

Thus, we present four analytical methods to distinguish mineral elements and environmental elements into positive and negative spectra based on depth profiling data using LIBS. It allows independent analysis of unknown environmental and mineral elements. When a laser is continuously shot at one point, a small amount of surface material is ablated. The effect of the environment on the surface will then disappear, thus revealing the composition of the mineral. This is presented as intensity variation in consecutive LIBS spectra. With increasing laser shots and depth of the laser crater, the intensity of the mineral elements gradually increased while the intensity of environmental elements gradually decreased. Thus, we investigated the intensity variation of each wavelength in several spectra obtained from our depth profiling process. The trend of signal intensity is presented by a single positive or negative value at each wavelength called trend value. The trend value makes it possible to create new spectrum representing a series of depth profiling, called a resultant spectrum. The resultant spectrum has an environmental elements with negative value and mineral elements with positive value. A positive spectrum means that the wavelength at which the signal intensity is increased with depth, indicating mineral element. A negative spectrum means that the wavelength at which the signal intensity is decreased with depth, indicating environmental element. A large magnitude of trend value of each wavelength in the spectrum suggests that the intensity varies rapidly depending on the depth. Thus, elements of environment and minerals can be easily found in these two spectra. In our experiment, minerals showed different spectra depending on environments they were exposed to. By using our new analytical methods, we investigated the unique effect of four different
environmental conditions (seawater, diesel oil, sulfuric acid, and air as control) on five minerals. These spectra were then subjected to principal component analysis (PCA) to validate the performance of our analytical methods. Consequently, we successfully extracted information of mineral and environmental elements from consecutive laser spectra using four proposed analytical methods.

**Experimental Setup and Methodologies**

*Experimental Setup*

A laser-induced breakdown spectroscopy system (RT250-Ec, Applied Spectra Inc.) was used as the LIBS equipment. This instrument was equipped with a Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser at wavelength of 1064 nm and pulse duration of 5–7 ns. Laser pulse energy was set at 20 mJ/pulse and a repetition rate was adjusted to 2 Hz. A six-channel charge-coupled device (CCD) spectrometer with a delay time of 1 μs and a gate width of 1.05 ms was used to cover the spectrum ranging from 190 nm to 1040 nm. The resolution of the spectrometer was from 0.10 nm to 0.12 nm. A sample was located in the chamber, which was mounted on an x, y, z stage. The stage enabled the chamber to move very delicately in a range of 300 mm in x-, y-, and z-axes. Uncoated quartz lens with focal length of 100 mm was used to focus the laser beam. Distance of the surface of the sample was adjusted to maximize LIBS spectra intensity. The focused laser was used to irradiate a sample surface perpendicularly in a chamber. Generated plasma light was collected to optical fiber through a focal lens with a focal length of 100 mm at an angle of 30° with laser beam and collected light passing to the spectrometer. The sample was placed on an aluminum plate. Experiments were carried out in the chamber. The pressure remained constantly at atmospheric pressure.

*Experimental Method*

We performed two experiments. The first experiment was surface analysis for investigating spectral changes by the environmental influence. Surface analysis was performed by irradiating a single laser pulse on a mineral surface at 50 points. Then the second experiment was performed, aimed at depth profiling to monitor the spectral changes with increasing depth. The depth profiling was performed by irradiating 100 laser pulses on a mineral surface at a single point. However, environmental effect on mineral samples can be different
depending on laser irradiation points because mineral sample surfaces are rugged and irregular. Some of them may have a lot of environmental elements while others do not. Therefore, in this experiment, spectral data were obtained at five arbitrary points for each experiment. Data from the 1st spectrum to the 100th spectrum were transformed into only one spectrum in four analytical methods at each point. We then averaged five calculated spectra.

Samples and Environments Preparation

Five mineral samples were purchased (Hansol Education Co.) and used in the experiment. Detailed information is shown in Table I. These minerals were comparatively earth-rich with different elemental compositions for sample diversity. The size of each mineral was about 4 cm x 4 cm x 4 cm at a main composition of 95% purity.

Four different environmental conditions were prepared as follows: All mineral samples were washed in distilled water before the experiment. To make seawater (NaCl), 150 ml of distilled water in beaker was mixed with natural salt at a concentration of 3.5% w/w, similar to real seawater concentration. For crude oil preparation, diesel oil (GS Caltex, Co.) consisting of saturated hydrocarbons and 25% of aromatic hydrocarbons was used as an alternative of crude oil. Atomic compositions of crude oil were: 83–87% C, 10–14% H, 0.1–2% N, 0.1–1.5% O, 0.5–6% S, and less than 0.1% metals. Mass fractions of diesel oil were 83–87% C and 10–14% H. To prepare sulfuric acid, sulfuric acid solution (H₂SO₄) of pH 4 was used. All samples were immersed in three liquid solutions for 24 hours. After that, samples were dried on aluminum plates in the laboratory for 24 hours at temperature of 25 °C and relative humidity of 25%. As a control, five samples of washed mineral were exposed to air for 24 hours and then were dried for 24 hours. For each of these five mineral samples, experiments were conducted under four differential conditions.

Table I. Chemical formulas and representative peaks of mineral samples.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Main peaks</th>
</tr>
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<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>Si (288.149 nm), Si (634.565nm), O (777.298 nm)</td>
</tr>
<tr>
<td>Azurite</td>
<td>Cu(OH)₂(CO₃)₂</td>
<td>Cu (510.543 nm), Cu (521.754 nm)</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
<td>Pb (368.370 nm), Pb (405.880 nm)</td>
</tr>
</tbody>
</table>
Principal Component Analysis (PCA)

In order to test the performance of the four analytical methods proposed in this study, we subjected spectra to PCA by dividing them into positive spectra and negative spectra. PCA is a statistical technique that can change high-dimensional data to low-dimensional data. Principal component analysis can linearly transform data into a new coordinate system so that the first principal component has the largest variance while the succeeding principal component (PC) has the next greatest variance. Each PC has constraints that are orthogonal to each other. PCA enables visual classification of samples by distributing them in such way so that sample differences can be presented the best. Score plot shows distribution of samples on PCs axes while loading plot is an indicator of what factors are important for each PC. In this work, The Unscrambler X 10.1 (Camo AS, Norway) was used to perform the PCA.

Results and Discussion

Raw Spectra Analysis

After exposing each mineral to four conditions, LIBS spectra were measured. The first LIBS spectra of mineral samples for four environments are shown in Figure 1. All spectra were averaged by five spectra to decrease intensity fluctuation and systematic error. Spectra were normalized by maximum intensity value. Each spectrum was offset by an increment of zero to three. Each major element was marked on the graph. Based on atomic emission line database of NIST wavelengths of main elements of mineral samples: Si (288 nm, 634 nm) and O (777 nm) in quartz, Cu (510 nm, 521 nm) in Azurite, Pb (368 nm, 405 nm, 500 nm) in Galena, Ca (393 nm, 487 nm, 526 nm, 558 nm) in calcite, Fe (373 nm, 495 nm) and O (777 nm) in magnetite as shown in Table I. 

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelengths</th>
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<tbody>
<tr>
<td>Pb</td>
<td>500.553 nm</td>
</tr>
<tr>
<td>Ca</td>
<td>(393.376 nm), (487.788 nm)</td>
</tr>
<tr>
<td></td>
<td>(526.988 nm), (558.844 nm)</td>
</tr>
<tr>
<td>C</td>
<td>(283.671 nm), O (777.298 nm)</td>
</tr>
<tr>
<td>Fe</td>
<td>(373.529 nm), (495.713 nm), O (777.298 nm)</td>
</tr>
</tbody>
</table>

Table I: Atomic emission line wavelengths for main elements of mineral samples.
To investigate the environmental effects, we performed PCA using the first spectrum of each mineral samples. The spectrum of first laser shot contains impact of environmental condition that the mineral was exposed to. By examining surface elements, information on environment of the mineral can be obtained. This makes it possible to classify minerals according to the environment that they are placed in. Even the same mineral can have different surface elements if it is exposed to different environments. Based on this assumption, there will be differences in LIBS spectra. We classified each spectrum through PCA using the first spectra. Although these minerals have the same compositions, after giving specific conditions, they are grouped according to their environmental condition by PCs. This means that each spectrum had difference compared to the original one due to the impact of a given environmental condition. Such difference can be used to infer the environment.

However, each LIBS spectrum has different intensity scales. To overcome this problem, preprocessing of data is necessary. Unit vector normalization was used to uniformly scale spectra for better analysis quality. Unit vector normalization is a way to set the square root of the sum of all components of the spectrum to one. All data analyses were proceeded after data preprocessing. In the PCA score plot as shown in Figure 2a, spectra of quartz exposed to four environmental conditions were grouped into different environments by three PCs. This shows that there is a difference in spectra depending on environments. Such difference can be used for environmental classification. PC loadings are shown in Figure 2b. PC loadings are how the wavelengths correlate to each PC. A positive loading indicates that a wavelength and a PC are positively correlated. For example, an increase of intensity of the wavelength implies an increase of the PC. A negative loading indicates that a wavelength and a PC are negatively correlated. For example, an increase of intensity of the wavelength implies a decrease of the PC. Based on the concept of PC loading, spectra of seawater condition are located at positive sides of PC2 and PC3 because Na signal (588 nm) has positive loading in PC2 and PC3. Spectra of diesel oil condition are located at negative sides of PC1 and PC2 but the positive side of PC3 because CN band (388 nm) has a negative loading in PC1 and PC2 but a positive value in PC3. Sulfuric acid condition is located on the positive side of PC1 because H signal (656 nm) on PC1 has a positive loading.
Figure 1. LIBS spectra of minerals after exposure to four different environmental conditions from first laser shot data.
Figure 2. (a) Score plot of first three PCs of four quarts after exposure to four different environmental conditions. (b) PCA loadings of the first three PCs.
In the spectra after exposure to seawater, concentrations of alkali and alkaline earth metals such as Na, Ca, K and Mg were increased greatly. This means that residues of seawater remained on the surface of the mineral while water was evaporated. In the spectra of diesel oil, CN band (388 nm) appeared. This is due to the combination of C in hydrocarbon fuels and N\textsubscript{2} in the air. In the spectra of sulfuric acid, H (656 nm) signal had a very high intensity. These results confirmed that LIBS spectrum was affected by the environmental condition and that the difference in spectrum was unique to each environment. This is because environmental elements will remain on the mineral surface and appear in the spectrum. Based on this, information on environmental condition of the mineral can be obtained. However, detection of Na on the surface of the mineral does not confirm that the mineral has been exposed to seawater or other salt condition. It may mean that the mineral itself contains Na element. Therefore, depth profiling is needed.

While the surface of mineral is affected by the environment, only pure elements of mineral sample will come out below the surface coating without showing environmental effects. Therefore, we analyzed how LIBS spectra changed as laser pulse progressed from the first laser shot to the last laser shot. For depth profiling, a hundred laser pulses were irradiated. Changes in intensity variation of quartz are shown in Figure 3. The x-axis is the number of laser shots while the y-axis is signal intensity averaged from five spectra. In Figure 3a, at the first spectra of quartz, signal of Na was measured to have the maximum. With increasing laser shot number, the signal of Na was steadily decreased by the about fortieth laser shot. However, for the other three cases, Na signal had relatively lower profile. This is because NaCl in seawater has remained on the surface. However, after several laser pulses, NaCl was ablated. Therefore, the influence of seawater residue disappeared with only information of the mineral left in the later spectra. The same tendency was observed in profile for CN band and hydrogen as shown in Figures 3b and 2c, respectively. In profile for silicon as shown in Figure 3d, Si signal as a signal of the main mineral element was increased after the lowest of its signal was observed in the first shot. Based on these results, initial few LIBS spectra will provide information about the environmental condition to which the sample had been exposed. After several laser shots, the original sample composition will appear, enabling the identification of the atomic composition of the mineral.

In depth profiling, spectrum changes were observed as the laser shot progressed. In the initial few spectra, both environmental and mineral elemental information came out at the same time. However, in later spectra, environmental information became blurred while pure
mineral information appeared. Differences between these two types of spectra could be seen as environmental influences. Based on such differences, it is also possible to predict unknown environmental element. Moreover, based on LIBS signal of a pure mineral, the composition of this mineral can be grasped.

However, these depth-profiling analyses are only possible if a specific environment is known in advance or intensity changes at certain wavelength can be predicted such as those in previous PCA loadings. However, PCA analysis using LIBS spectra of five mineral samples from first laser shot did not give any environmental information due to the complexity of various mineral elements and environmental elements. It is hard to know such things about unknown environmental conditions of minerals in real fields. Therefore, we presented four analytical methods to distinguish mineral and environmental elements from a series of consecutive spectra.
Figure 3. Signal variation of quartz in four different conditions of (a) Na (588.911 nm), (b) CN (388.328 nm), (c) H (656.249) and (d) Si (634.565 nm).
Delta Analyses: Two Types

In the following sections, four types of trend values are defined in different ways. The trend value indicates how much the intensity increase or decrease at a wavelength during depth profiling. By plotting the trend values with respect to wavelengths, a new resultant spectrum of depth profile data can be created. In the spectrum, increasing intensity will have positive value and decreasing intensity will have negative value at their wavelength.

The first method is delta analysis 1. We defined a value called $\Delta I_k$ (delta ratio) to determine how much the intensity varied at each wavelength from $k$th spectrum to the next spectrum and it is defined according to Eq. 1, delta analysis 1. $I_k$ is an intensity at a specific wavelength in the $k$th spectrum and $S_n$ is the sum of $\Delta I_k$. If the intensity increases in the next spectrum, $\Delta I_k$ will have a positive value. However, if it decreases, $\Delta I_k$ will have a negative value.

$$I_k = \frac{I_{k+1}}{I_k} (k = 1,2,...,n)$$

$$S_n = \sum_{k=1}^{n-1} \Delta I_k$$ (1)

If there are 100 consecutive spectra, there will be 99 $\Delta I_k$ between spectra. The sum of these $\Delta I_k$ is set as a representative of how much change of the intensity is at this wavelength. However, this process is unsuitable for all wavelengths because the denominator has an intensity value. If noise value other than the peak value is input to the denominator, the value of $\Delta I$ is divergent. Therefore, we need to set the noise value so that we can ignore all intensities below a certain value. In delta analysis 1, the noise level was set at 500. Instead of calculating $\Delta I_k$ for intensities of all wavelengths, values are only calculated for peaks. The principle of selecting peaks is the same as the principle set for local maximum. If the intensity is greater than intensities on either side, the wavelength is chosen as the peak.

Therefore, only values selected by peak were calculated to determine their $\Delta I_k$. This results in an $S_n$ value, which is the sum of all $\Delta I_k$ for each wavelength. By drawing the spectrum, it is possible to obtain the tendency of increasing or decreasing in wavelength in the form of spectrum.

When graph was drawn in this way, the $S_n$ value of Na (588.911 nm) was positive for seawater in all mineral samples. This is because signal intensities are locally increased or decreased in spite of the overall decreasing graph. Although the same amount is changed, when a larger intensity enters the denominator before the decrease, the $\Delta I_k$ value becomes
smaller. However, when increase occurs and a smaller intensity enters the denominator, the $\Delta I_k$ value becomes bigger. Consequently, the $S_n$ value tends to have a positive value.

Thus, when the same amount changes, $\Delta I_k$ is newly defined so that the sum of $\Delta I_k$ becomes zero as shown in Eq. 2, delta analysis 2. If the denominator is set as the average of the back and forth intensities, the sum of $\Delta I_k$ becomes zero when increasing and decreasing have the same quantity. In delta analysis 2, if the intensity suddenly increases, it has a large delta ratio value. However, when it goes down to the same point, it has a small delta ratio value. In this case, if the intensity bounces or vibrates for a while, it will have a positive bias. For this reason, the delta 2 scheme is required. In delta analysis 2, when the intensity suddenly increases and then returns to its original position, the sum of values of delta ratio is equal in magnitude but opposite in sign. In this case, it is possible to obtain a stable delta sum without generating an error even when sudden change of intensity occurs during the depth profiling process. In other words, delta 1 scheme is biased toward positive while the delta 2 scheme is neutral, the noise level is set to 300.

$$I_k = \frac{I_{k+1} - I_k}{(I_{k+1} + I_k)/2} (k = 1, 2, ..., n \ 1) \sum_{k=1}^{n-1} I_k (2)$$

In this case, elements of the mineral will come out in positive spectra. As a result, the problem that the environmental element observed in delta analysis 1 has a positive value was solved. Extracting elements of the mineral was successful. However, negative spectra were very noisy, making it hard to find elements of the environment. This is caused by noise level. When intensity decreases, the delta intensity ratio has a negative value. However, when intensity decreases below the noise level, delta intensity ratio is set to have a value of zero. For this reason, $S_n$ value has a negative value at a wavelength when intensities pass the noise level. Although this method could sort out elements of the mineral, it was hard to find environmental elements.

**Differential Analysis**

Until now, we have used all data from the first to the 100th spectra. Instead, an easier and simpler way is subtracting the first spectra from the last spectra. Ideally, if an intensity has a
maximum value in the first spectrum and a minimum value in the last spectrum, the subtracted value has a negative value. This means that the intensity of wavelength is decreased and the element suggests environmental elements. Using this method, calculated spectra have stable shape with almost no noise because they are calculated with two spectra. However, in some spectra, it can be seen that elements of the mineral have negative values. The reason for this is that intensities of LIBS spectra have relatively high variations in just two spectra. Therefore, it is rough to analyze them with only two data points.

Slope Analysis
Finally, we plotted a linear fitting curve for each wavelength to determine the overall intensity trend. The linear fitting slope was designated as a representative value indicating the tendency of each wavelength. For example, in a sample of SiO$_2$ mineral after exposure to seawater condition, we will see 634 nm as a representative wavelength of Si. Figure 4 shows changes in intensities from the first to the one-hundredth laser shots. The intensity at 634 nm showed very low signal intensity in the first laser shot. Its signal intensity gradually increased as the number of laser shots increased as shown in Figure 4a. When we linearly approximated this, we could see that it had a positive slope. The depth profile of 588 nm, which is the wavelength representing Na, is shown in Figure 4b. The shape of the profile has the form of exponentially decaying. However, linear approximation here has a negative slope at $-156.3$. What is important here is the sign of the slope. If the sign of the slope is positive, it means that the intensity of the signal is increased as depth profile progresses. It can be calculated very easily for all wavelengths.
Figure 4. Linear fitting curve of the depth profiles of (a) Si (643 nm) and (b) Na (588 nm).
Verification of the Results Using Principal Component Analysis (PCA)

To verify that each positive spectrum obtained by the four methods actually represents elements of the mineral, PCA was performed using positive parts of resultant spectra. First of all, PCA using raw data of the first spectra of five mineral samples was performed in Figure 5a. The result did not reveal any patterns of mineral and environmental elements due to the mixed data of mineral and environments. Figure 5b–e shows the PCA score plot using positive spectra obtained from four analytical methods. Calcite, galena, and magnetite were well classified in Figure 5b, c. However, quartz and azurite were found in the same group as shown in Figure 5b, c. Azurite and magnetite were also in the same group in Figure 5d. However, all minerals were clearly classified except for one magnetite and one galena data points in Figure 5e. As a result, four methods extracted some elements of the mineral. However, the slope analysis seems to have more distinguishing performance of mineral elements than other methods.

In addition, to verify that each negative spectrum obtained by the four methods represents environmental elements, PCA was performed using negative parts of resultant spectra. The PCA score plot using negative spectra implies extraction of environmental elements by the four methods. Using delta analysis 1, delta analysis 2, and differential analysis, the environmental groups are shown to be overlapping. Nevertheless, a certain pattern of each environmental group, which were not seen using raw spectra, appeared in the PCA plot using the slope analysis in Figure 5f. This implies that slope analysis extracted environmental elements from depth profiling data.
Figure 5. (a) PCA results using the first LIBS spectra of five minerals. Comparison of PCA results using positive parts of resultant spectra from (b) delta analysis 1, (c) delta analysis 2, (d) differential analysis, and (e) slope analysis to verify distinguishing performance of
mineral elements. (f) PCA results using negative parts of resultant spectra form slope analysis to verify distinguishing performance of environmental elements.

Resultant Spectrum Using Slope Analysis

Resultant spectra of quartz using slope analysis in four environmental conditions are shown in Figure 6. Figure 6a shows that the slope value has positive peaks at 634.504 nm and 636.904 nm in all cases, except the air case. The reason is that the air case does not give large variation of Si signal because it has no coating on the surface. These positive peaks mean that the Si signal intensity has gradually increased at that wavelength by removing surface materials. On the other hand, slope values are usually zero except peaks. This means that the intensity is not much increased or decreased with increasing number of laser pulses, suggesting no change in that wavelength. Figure 6b shows the difference in Na signal in four environmental conditions. Na (588.911 nm and 589.544 nm) had a large negative slope value in the seawater condition, a lower value in diesel oil condition, and a value close to zero in the remaining cases. Similarly, the CN band (388.328 nm) had peaks only in the case of diesel oil, as shown in Figure 6c. This means that the signal from the early laser pulse is very large. However, signal intensity is gradually decreased. That is, the wavelength of the external matter remaining on the surface has a negative value. As an example, total spectrum of SiO$_2$ seawater is shown in Figure 6d. Therefore, it is possible to find what materials are present on the surface of this mineral from negative peaks and major elements of the mineral from positive peaks. Resultant spectra of all minerals by four analytical methods were summarized in the supplementary material. Each spectrum was obtained by averaging five data.
Figure 6. The resultant spectrum of quartz obtained by slope analysis near (a) Si peaks, (b) Na peak, (c) CN peak and (d) total spectrum.
Conclusion
Four analytical methods to distinguish mineral and environmental elements into positive and negative spectra based on the depth profiling data using LIBS have been proposed. The intensity of environmental elements gradually decreased while the intensity of mineral elements gradually increased by a deeper laser ablation. By plotting the trend values with respect to wavelengths, a new spectrum of the depth profile was obtained. The spectrum has mineral elements as positive values and environmental value as negative values. In addition, the proposed methods can facilitate LIBS analysis by replacing the raw depth profiling data with the newly attained spectrum.

Conflict of Interests
The Authors declare that there is no conflict of interest.

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Supplemental Material
All supplemental material mentioned in the text, consisting of Figures S1–S4, is available in the online version of the journal.

References


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Figure S1. Delta analysis 1, spectra shown with offset values from 0 to 3.
Figure S2. Delta analysis 2, spectra shown with offset values from 0 to 3.
Figure S3. Differential analysis, spectra shown with offset values from 0 to 3.
Figure S4. Slope analysis, spectra shown with offset values from 0 to 3.