

Preliminary study of elemental detection using LIBS from orbit on airless planetary surfaces

K. Nagamine^{*a}, K. Tsuno^a, H. Yashiro^a, M. Maruyama^a, S. Watanabe^a, T. Fukushima^a,
T. Ogawa^b, S. Wada^b

^aOrbital Lasers Co., Ltd, Kanagawa Science Park (KSP), 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan; ^bRIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

ABSTRACT

Characterizing the elemental composition of planetary and asteroid surfaces is important for understanding the formation and geologic evolution of planetary bodies and for assessing resource distributions. Planetary LIBS measurements have mainly been limited to short-range observations by landers and rovers, whereas LIBS from orbit could enable elemental measurements over wide areas without requiring a landing. In this study, LIBS experiments under vacuum conditions using hydroxyapatite (HAp) and a model for orbital observations were used to evaluate the feasibility of elemental detection on airless planetary surfaces. Ca I and Ca II emission was measured at laser fluences of 3.8–53.8 J/cm². The plasma continuum was estimated from absolutely calibrated spectra, and five Ca emission lines were quantified by Voigt-profile fitting. The fluence dependence of the line and continuum radiances was represented using a model developed in this study, which was then applied to orbital observation conditions to calculate the signal-to-noise ratio (SNR). For high Ca abundance, the maximum observation range was primarily limited by the plasma formation threshold at the target surface, with detection at kilometer-scale distances indicated under representative system parameters. In contrast, for 0.1 wt% Ca, assuming linear scaling of Ca emission-line radiance with Ca abundance, shot noise from the plasma continuum dominated near the detection limit. These results quantitatively show how plasma formation and plasma-continuum shot noise can limit LIBS observations from orbit.

Keywords: laser-induced breakdown spectroscopy (LIBS), planetary exploration, elemental analysis, remote sensing

*kenshin.nagamine@orbital-lasers.com; orbitallasers.com/en/

1. INTRODUCTION

Determining the mineralogical and elemental composition of planetary surfaces is an important objective in planetary exploration, and a variety of analytical techniques have been used, including Raman spectroscopy, X-ray fluorescence spectroscopy, and gamma-ray and neutron spectroscopy. Among these techniques, laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopic technique in which a focused laser beam ablates the sample and generates a plasma, and the elemental composition is determined from the optical emission spectrum of the plasma. LIBS requires no sample preparation and enables the simultaneous detection of a wide range of elements, including light elements. LIBS has been successfully implemented in planetary exploration missions, including ChemCam on the Curiosity rover, SuperCam on the Perseverance rover, and LIBS on the Pragyan rover of Chandrayaan-3, demonstrating its applicability to planetary exploration [1-3].

To date, the use of LIBS in planetary exploration missions has been primarily limited to short-range measurements from rovers on planetary surfaces. LIBS observations from orbit could enable measurements of elemental distributions over large areas and provide a complementary capability to sample-return missions and surface exploration. Potential applications include remote analysis of asteroid surface composition during flybys and large-area elemental mapping from orbit around airless planetary bodies, including the Moon.

Stand-off LIBS has been investigated for Mars exploration. Laboratory measurements under simulated Martian atmospheric conditions have demonstrated LIBS measurements of metal and rock samples at target distances of 3–12 m [4]. Stand-off LIBS has also been implemented in ChemCam on the Curiosity rover and SuperCam on the Perseverance

rover, with measurements at ranges of several meters [2,5]. Extending LIBS from meter-scale stand-off measurements to orbital distances, however, places much more stringent requirements on the transmitter and receiver optics. To our knowledge, quantitative evaluations of LIBS at orbital distances based on experimentally measured and absolutely calibrated emission-line and plasma-continuum radiances obtained under vacuum conditions have not been reported.

In this study, hydroxyapatite (HAp) was used as the target material, and the feasibility of elemental detection by long-range LIBS observations from orbit was evaluated primarily using Ca emission lines. To simulate the vacuum environment of an airless planetary surface, Ca emission lines and the plasma continuum from laser-induced plasma were measured under vacuum conditions, and their pulse-integrated radiances were modeled as a function of laser fluence. The resulting model based on the experimental measurements was then applied to orbital observation conditions. The detectability of the Ca emission lines was evaluated in terms of the signal-to-noise ratio (SNR) by calculating the signal and noise components at the detector.

2. EXPERIMENTAL SETUP AND CONDITIONS

Hydroxyapatite (HAp), whose composition is well defined, was used as the experimental target. The chemical formula of HAp is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and its Ca content is 39.9 wt%. Within the wavelength range of the spectrometer used in this study, Ca exhibits several relatively strong Ca I and Ca II emission lines suitable for quantitative analysis. Therefore, Ca was selected as a representative element for evaluating the feasibility of elemental detection using LIBS from orbit.

Figure 1 shows the experimental setup. The laser beam was focused onto the HAp surface using a plano-convex lens with a focal length of 500 mm to generate a laser-induced plasma. The laser fluence at the target surface was varied by changing the laser pulse energy and by translating the plano-convex lens along the optical axis to change the laser spot size on the target surface. The HAp target was tilted by 30 deg with respect to the laser optical axis, resulting in an elliptical laser spot on the target surface. The laser spot size was defined based on the $1/e^2$ intensity contour. The experimental conditions are summarized in Table 1. The pressure during the experiments was maintained below 2.5×10^{-2} Pa.

Plasma emission was collected using a fiber-coupled cosine corrector positioned along the surface normal of the target. A fused-silica cover glass was placed in front of the cosine corrector to prevent ablated particles from depositing on its surface and reducing its transmission. The transmittance of the cover glass was approximately constant at 0.92 over the wavelength range of the spectrometer. Because laser-induced plasma expands predominantly along the target normal direction [6,7], the plasma emission was observed along the target normal in the present configuration. An LR1-B spectrometer (ASEQ Instruments) was used for the measurements.

Absolute radiometric calibration of the spectroscopic system was performed using an HL-3 plus calibration light source (Ocean Optics), and a wavelength-dependent sensitivity correction factor was obtained over the wavelength range of 350–1230 nm. The spectrometer counts were converted to pulse-integrated spectral radiance per laser pulse using the following equation:

$$L_{\lambda}^{\text{abs}} = \frac{C_{\lambda} S_{\lambda}}{T_{\text{cg}} \Omega_{\text{src}} f_{\text{laser}} t_{\text{exp}}} \quad (1)$$

where C_{λ} is the spectrometer count, S_{λ} is the wavelength-dependent sensitivity correction factor, and T_{cg} is the transmittance of the cover glass. Because the cover-glass transmittance was approximately constant over the wavelength range of the spectrometer, $T_{\text{cg}} = 0.92$ was used. Ω_{src} is the solid angle subtended by the laser-irradiated area on the HAp target as viewed from the cosine corrector. For the present experimental geometry, it was approximated as $\Omega_{\text{src}} \approx A_{\text{spot}}^{\text{exp}} / d_{\text{det}}^2$, where $A_{\text{spot}}^{\text{exp}}$ is the laser spot area on the target surface and d_{det} is the distance from the laser-irradiated position to the cosine corrector. Here, f_{laser} is the laser repetition rate and t_{exp} is the spectrometer exposure time. In this study, $f_{\text{laser}} = 20$ Hz and $t_{\text{exp}} = 0.5$ s; therefore, 10 laser pulses were accumulated in each spectrum. The pulse-integrated spectral radiance obtained from Eq. (1) has units of $\mu\text{J}/(\text{cm}^2 \text{ sr nm pulse})$.

Time-resolved measurements of the temporal evolution of the plasma emission were not performed in this study. Instead, the analysis was based on the spectral radiance integrated over the plasma emission generated by each laser pulse. Accordingly, the subsequent evaluation of LIBS detectability from orbit was also based on pulse-integrated emission.

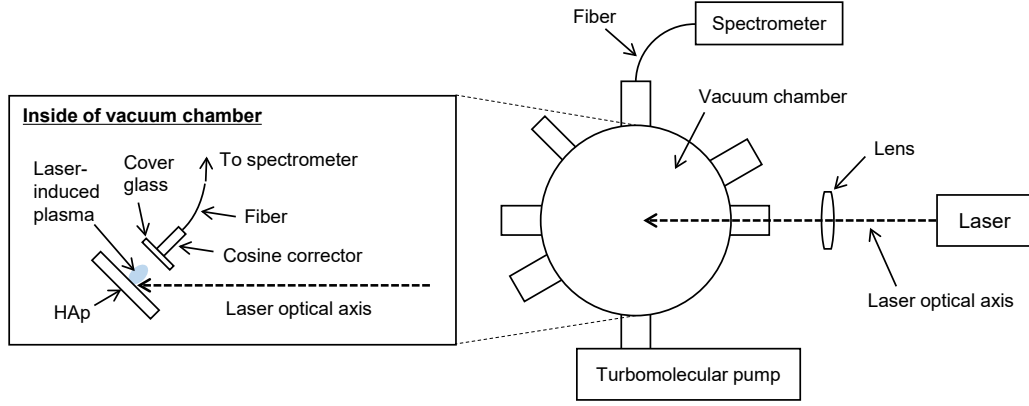


Figure 1. Experimental setup for LIBS measurements of the HAp target under vacuum conditions.

Table 1. Experimental parameters and measurement conditions for LIBS measurements of the HAp target under vacuum conditions.

Parameter	Symbol	Value	Unit
Laser wavelength	λ_{laser}	1064	nm
Pulse width	-	10	ns
Laser energy	-	25, 55, 84	mJ
Spot area	$A_{\text{spot}}^{\text{exp}}$	0.16, 0.42, 0.66	mm ²
Fluence	F	3.8 – 53.8	J/cm ²
Pulse repetition rate	f_{laser}	20	Hz
Exposure time	t_{exp}	0.5	s
Distance between HAp and cosine corrector	d_{det}	12	mm
Cover-glass transmittance	T_{cg}	0.92	-
Target tilt angle relative to laser optical axis	-	30	deg
Pressure during experiment	-	$< 2.5 \times 10^{-2}$	Pa

3. RESULTS AND DISCUSSION

This section first presents the LIBS spectra measured under vacuum conditions and their dependence on laser fluence, followed by an evaluation of elemental detectability using LIBS from orbit based on the resulting emission model.

3.1 Experimental spectra and fluence dependence

Figure 2 shows a representative spectrum converted to pulse-integrated spectral radiance using the absolute radiometric calibration described by Eq. (1). The spectrum was measured at a laser pulse energy of 84 mJ, a laser spot area of 0.16 mm², and a laser fluence of 53.8 J/cm². Multiple Ca I and Ca II emission lines were observed in the measured spectrum. In this study, five relatively strong emission lines within the wavelength range of the spectrometer were selected for quantitative analysis: Ca II at 370.74, 373.80, 393.49, and 396.99 nm, and Ca I at 422.80 nm.

In addition to the Ca emission lines, the measured spectrum contained broadband continuum emission from the laser-induced plasma. The continuum spectrum B_{λ} was therefore estimated using the 4S peak-filling algorithm [8]. Denoting the absolutely calibrated spectrum by L_{λ}^{abs} , the continuum-subtracted spectrum $L_{\lambda}^{\text{corr}}$ is given by

$$L_{\lambda}^{\text{corr}} = L_{\lambda}^{\text{abs}} - B_{\lambda}. \quad (2)$$

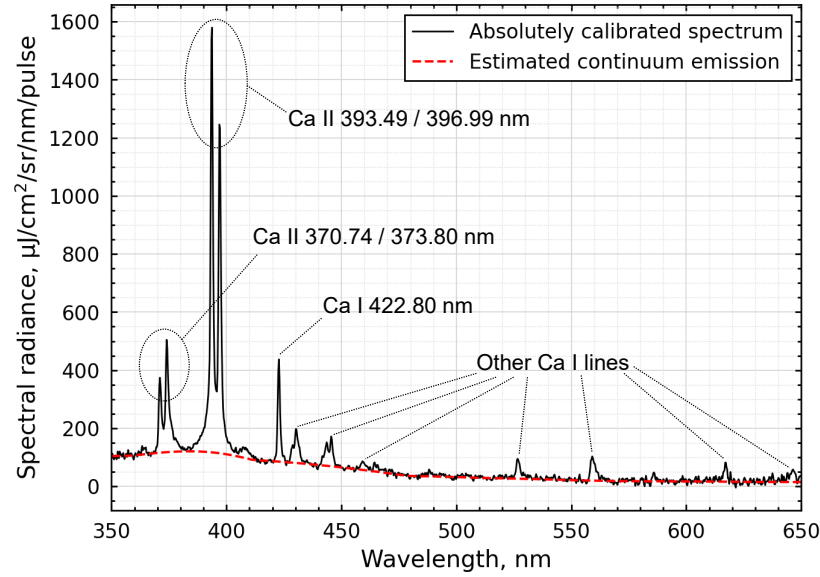


Figure 2. Absolutely calibrated pulse-integrated spectral radiance and plasma continuum estimated using the 4S algorithm. The laser pulse energy, spot area, and laser fluence were 84 mJ, 0.156 mm², and 53.83 J/cm², respectively.

Figure 2 also shows the absolutely calibrated spectrum together with the continuum spectrum estimated using the 4S algorithm. The continuum emission extended over the entire measured wavelength range, and its spectral radiance varied with wavelength.

To quantify the radiance of each emission line, the continuum-subtracted spectrum $L_{\lambda}^{\text{corr}}$ was fitted with Voigt profiles. A Voigt profile is the convolution of Gaussian and Lorentzian profiles. In this study, the FWHM of the Gaussian component was fixed at 0.3 nm, which was assumed to represent the instrumental broadening of the spectrometer, while the Lorentzian width, peak amplitude, and a common wavelength shift were treated as fitting parameters. Because the wings of Ca II 370.74 nm and Ca II 373.80 nm overlap, as do those of Ca II 393.49 nm and Ca II 396.99 nm, each pair of emission lines was fitted simultaneously.

Figure 3 shows representative results of the Voigt-profile fitting. For both Ca II doublets and the Ca I 422.80 nm line, the fitted profiles reproduced the measured line shapes reasonably well.

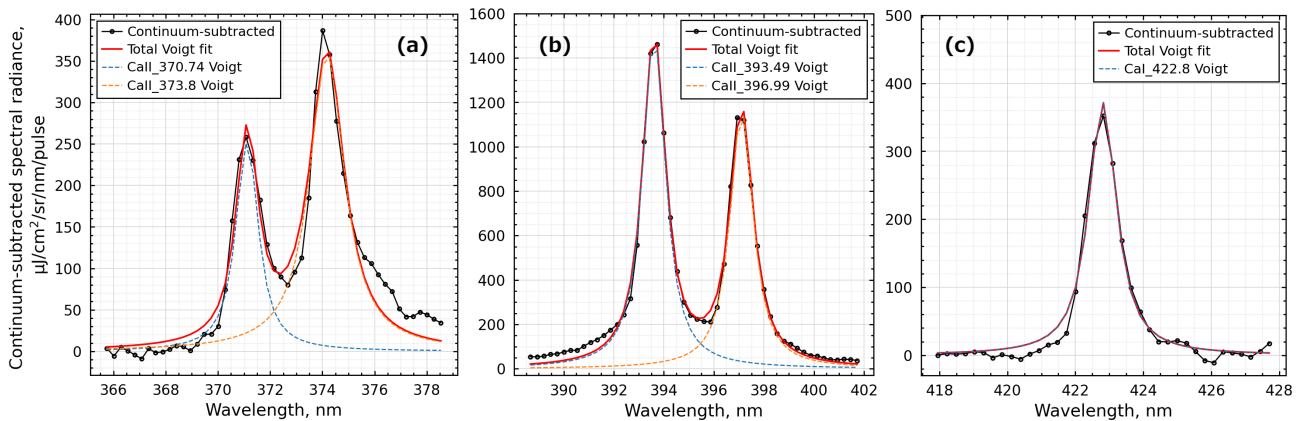


Figure 3. Continuum-subtracted spectra and Voigt fits for representative Ca emission lines: (a) Ca II 370.74 nm and Ca II 373.80 nm, (b) Ca II 393.49 nm and Ca II 396.99 nm, and (c) Ca I 422.80 nm. The laser pulse energy, spot area, and laser fluence were 84 mJ, 0.156 mm², and 53.83 J/cm², respectively.

The integrated radiance of emission line i , $L_{\text{line},i}$, was obtained by integrating its fitted Voigt component $V_i(\lambda)$ over a wavelength range of ± 1 nm around the fitted center wavelength λ_i , as given by Eq. (3):

$$L_{\text{line},i} = \int_{\lambda_i - 1\text{nm}}^{\lambda_i + 1\text{nm}} V_i(\lambda) d\lambda. \quad (3)$$

Similarly, the integrated continuum radiance $L_{\text{cont},i}$ associated with each emission line was calculated over the same wavelength range, as given by Eq. (4):

$$L_{\text{cont},i} = \int_{\lambda_i - 1\text{nm}}^{\lambda_i + 1\text{nm}} B_\lambda d\lambda. \quad (4)$$

The same wavelength interval of $\Delta\lambda = 2$ nm was also used in the subsequent calculations of the line signal, plasma continuum, solar background, and number of detector pixels.

To describe the dependence of the line and continuum radiances on laser fluence, we introduced the following model incorporating a fluence threshold:

$$L_{j,i}^{\text{model}} = C_{j,i} F \eta_{j,i}(F), \quad (5)$$

$$\eta_{j,i}(F) = \begin{cases} 0, & F \leq F_{\text{th}}, \\ 1 - \exp\left(-\frac{F - F_{\text{th}}}{F_{c,j,i}}\right), & F > F_{\text{th}}. \end{cases} \quad (6)$$

Here, j denotes either the line or continuum component, i denotes the Ca emission line of interest, $C_{j,i}$ is a scaling coefficient, and $F_{c,j,i}$ is a characteristic fluence describing the rise of the emission response. The factor $\eta_{j,i}$ is an empirical response factor describing the increase in emission above the threshold. In this model, the radiance is set to zero for $F \leq F_{\text{th}}$ and gradually increases above the threshold. At high fluence, $\eta_{j,i}$ approaches unity, and $L_{j,i}^{\text{model}}$ therefore becomes approximately proportional to the laser fluence.

In the present experiments, plasma formation was not observed at $F = 3.80$ J/cm², whereas it was observed at $F = 5.91$ J/cm². Based on these observations, the plasma formation threshold was set to $F_{\text{th}} = 5.0$ J/cm², which lies between these two measured fluences, and was fixed for all emission-line and continuum components in the fitting. Thus, $C_{j,i}$ and $F_{c,j,i}$ were the only free parameters.

Figure 4 shows the integrated line and continuum radiances for Ca II 370.74 nm, Ca II 393.49 nm, and Ca I 422.80 nm as functions of laser fluence, together with the fitted models. The data points represent the mean values of repeated measurements under the same experimental conditions, and the error bars indicate the sample standard deviation. The fitted models reproduced the observed rise of both the line and continuum radiances with laser fluence reasonably well.

The line-to-continuum ratio differed among the emission lines owing to differences in both the line radiance and the local continuum level. In particular, for Ca II 393.49 nm, the line radiance was substantially higher than the continuum radiance. In contrast, for Ca II 370.74 nm, the relative contribution of the continuum was larger than for the other two lines, and the line and continuum radiances were comparable under some experimental conditions near the threshold.

The fitting parameters and coefficients of determination for the line and continuum components are summarized in Table 2. The scaling coefficient $C_{\text{line},i}$ differed among the emission lines, reflecting differences in their absolute line radiances. In contrast, $C_{\text{cont},i}$ was relatively similar at the wavelengths of the five emission lines considered in this study, indicating that the continuum radiance did not vary substantially over this wavelength range. Both $F_{c,\text{line},i}$ and $F_{c,\text{cont},i}$ were of the same order of magnitude across the analyzed wavelengths, indicating broadly similar rising trends with laser fluence.

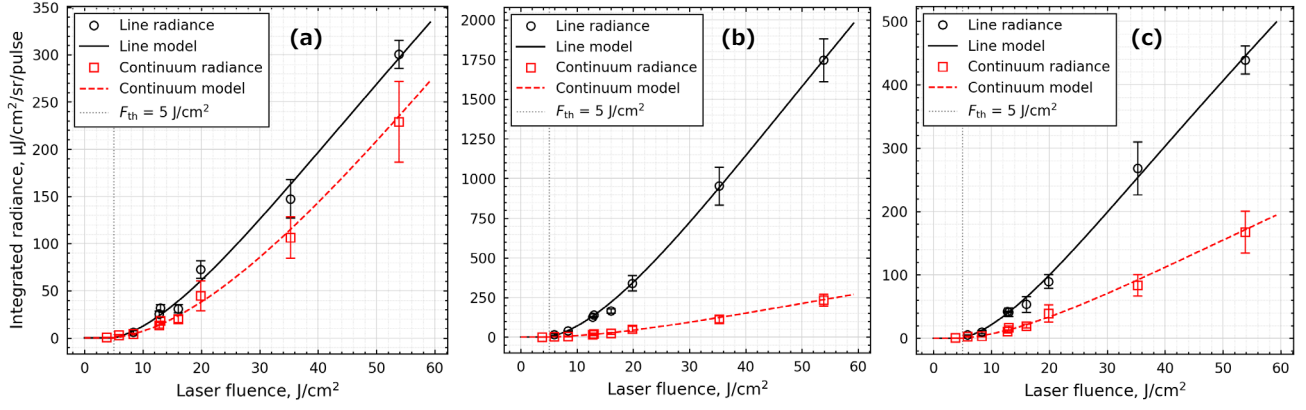


Figure 4. Integrated line and plasma-continuum radiances as functions of laser fluence, together with the fitted models: (a) Ca II 370.74 nm, (b) Ca II 393.49 nm, and (c) Ca I 422.80 nm.

Table 2. Fitting parameters and coefficients of determination for the Ca line and plasma-continuum radiance models.

Emission line	$C_{\text{line},i}$, [$\mu\text{J}/\text{J}/\text{sr}$]	$F_{\text{c,line},i}$ [J/cm^2]	R_{line}^2	$C_{\text{cont},i}$, [$\mu\text{J}/\text{J}/\text{sr}$]	$F_{\text{c,cont},i}$ [J/cm^2]	R_{cont}^2
Ca II 370.74 nm	6.3	21.8	0.98	6.4	42.1	0.95
Ca II 373.80 nm	10.4	15.7	0.98	6.2	39.2	0.95
Ca II 393.49 nm	37.3	24.2	0.99	5.3	28.4	0.96
Ca II 396.99 nm	30.1	26.7	0.99	5.1	27.2	0.95
Ca I 422.80 nm	8.9	18.3	0.98	3.7	24.7	0.93

3.2 Analysis of LIBS detectability from orbit

The fluence-dependent models of the line and continuum radiances obtained from the experiments were applied to LIBS observations from orbit. For a given laser fluence, the pulse-integrated radiance was assumed to be independent of the laser spot area. Therefore, the line and continuum radiances for orbital observations were calculated by substituting the laser fluence at the target surface, F_{orbit} , into Eqs. (5) and (6). The transmitted laser beam was assumed to have a Gaussian profile with a $1/e^2$ beam diameter equal to the telescope aperture diameter. Wavefront aberrations in the transmit optics were accounted for using the Strehl ratio SR , with the corresponding reduction in peak irradiance represented by an increase in the effective spot diameter. Under these assumptions, for a spacecraft-to-target distance r , laser wavelength λ_{laser} , telescope aperture diameter D_{opt} used for both transmission and reception, and laser beam quality factor M^2 , the effective $1/e^2$ laser spot diameter at the target surface is given by

$$d_{\text{spot}} = \frac{4\lambda_{\text{laser}} r M^2}{\pi D_{\text{opt}} \sqrt{SR}}. \quad (7)$$

The laser spot area and laser fluence at the target surface are then given by $A_{\text{spot}}^{\text{orbit}} = \pi d_{\text{spot}}^2/4$, $F_{\text{orbit}} = E_L/A_{\text{spot}}^{\text{orbit}}$, where E_L is the laser pulse energy.

As a first-order approximation for targets with different Ca contents, the radiance of each Ca emission line was assumed to scale linearly with the Ca mass fraction. Let $w_{\text{Ca(HAp)}} = 39.9\%$ be the Ca mass fraction in HAp and w_{Ca} the Ca mass fraction of the target. The radiance of each Ca emission line is then given by

$$I_{\text{line},i}^{\text{orbit}}(F_{\text{orbit}}, w_{\text{Ca}}) = \frac{w_{\text{Ca}}}{w_{\text{Ca(HAp)}}} L_{\text{line},i}^{\text{model}}(F_{\text{orbit}}). \quad (8)$$

In contrast, the plasma continuum does not arise solely from Ca and depends on the electron density and electron temperature of the plasma, as well as the composition of the target material. Therefore, the continuum radiance was assumed to remain unchanged from that measured for HAp when the Ca content was reduced. Accordingly, the results for 0.1 wt% Ca do not represent an experimentally measured detection limit using an actual sample. Rather, they are model predictions based on the assumptions that the Ca emission-line radiance scales linearly with Ca content and that the plasma continuum remains unchanged. The continuum radiance used for orbital observations is therefore given by

$$L_{\text{cont},i}^{\text{orbit}}(F_{\text{orbit}}) = L_{\text{cont},i}^{\text{model}}(F_{\text{orbit}}) \quad (9)$$

The numbers of photoelectrons generated at the detector by the emission line of interest and by the plasma continuum within the same 2-nm wavelength interval are given by

$$N_{j,i} = L_{j,i}^{\text{orbit}} A_{\text{spot}}^{\text{orbit}} \Omega_{\text{sat}} T_{\text{opt}} \eta_{\text{QE}} \frac{\lambda_i}{hc} \quad (10)$$

where T_{opt} is the transmission of the receiver optics, η_{QE} is the detector quantum efficiency, λ_i is the wavelength of the emission line of interest, h is the Planck constant, and c is the speed of light. The solid angle subtended by the telescope aperture as viewed from the target was approximated as $\Omega_{\text{sat}} = \pi D_{\text{opt}}^2 / 4r^2$.

For the background due to sunlight, the heliocentric distance was assumed to be 1 AU and the target surface was assumed to be Lambertian. Let $E_{\odot,\lambda}$ be the solar spectral irradiance at 1 AU, R_λ the surface reflectance, τ the detection gate time, and $\Delta\lambda$ the spectral bandwidth. The number of photoelectrons generated by sunlight reflected from the target surface is given by

$$N_{\text{sun},i} = \frac{E_{\odot,\lambda} R_\lambda}{\pi} \Delta\lambda \tau A_{\text{FoV}}^{\text{orbit}} \Omega_{\text{sat}} T_{\text{opt}} \eta_{\text{QE}} \frac{\lambda_i}{hc}. \quad (11)$$

To account for pointing error and jitter during the round-trip light time, the diameter of the receiver field of view (FoV) at the target surface was set to ten times the laser spot diameter. The corresponding FoV area was therefore 100 times the laser spot area.

In this analysis, $\Delta\lambda = 2.0$ nm and $\tau = 100$ μs were used. Over the wavelength range considered, the optical transmission, detector quantum efficiency, solar spectral irradiance, and surface reflectance were each approximated as constant. The other parameters used for the orbital observation analysis are summarized in Table 3.

The single-shot SNR of each emission line was evaluated by including photon shot noise from the emission line, plasma continuum, and reflected sunlight, as well as detector readout noise:

$$\text{SNR}_i = \frac{N_{\text{line},i}}{\sqrt{N_{\text{line},i} + N_{\text{cont},i} + N_{\text{sun},i} + n_{\text{pix}} \sigma_{\text{read}}^2}} \quad (12)$$

Here, $N_{\text{line},i}$, $N_{\text{cont},i}$, and $N_{\text{sun},i}$ also represent the corresponding Poisson shot-noise variances. n_{pix} is the number of detector pixels over which the signal is integrated, and σ_{read} is the readout noise per pixel. Assuming a spectral sampling of 0.2 nm/pixel, a spectral bandwidth of 2.0 nm, and one pixel in the spatial direction, $n_{\text{pix}} = 10$ was used in this analysis.

Figure 5(a) shows the single-shot SNR as a function of spacecraft-to-target distance for a laser pulse energy of 1 J. For the reference case corresponding to the Ca content of HAp, 39.9 wt%, the SNR of each emission line increased rapidly once the laser fluence exceeded the plasma formation threshold. Under the conditions assumed in this analysis, the distance at which $F_{\text{orbit}} = F_{\text{th}}$ for a laser pulse energy of 1 J was approximately 2.2 km. Thus, the maximum detection range for this reference case was primarily limited by the fluence threshold required for plasma formation.

Table 3. Laser, optical, detector, and observation parameters used for the analysis of LIBS detectability from orbit.

Parameter	Symbol	Value	Unit
Telescope aperture diameter	D_{opt}	1.0	m
Laser beam quality factor	M^2	1.2	
Strehl ratio	SR	0.5	-
FoV area at target surface	$A_{\text{FoV}}^{\text{orbit}}$	$100 A_{\text{spot}}^{\text{orbit}}$	m^2
Receiver optical transmission	T_{opt}	0.5	-
Quantum efficiency	η_{QE}	0.8	-
Solar spectral irradiance at 1 AU	$E_{\odot,\lambda}$	1.5	$\text{W}/\text{m}^2/\text{nm}$
Surface reflectance	R_{λ}	0.3	-
Detection bandwidth	$\Delta\lambda$	2	nm
Detection gate time	τ	100	μs
Fluence threshold	F_{th}	5	J/cm^2
Spectral sampling	-	0.2	nm/pixel
Number of pixels integrating spectral line	n_{pix}	10	pixel
Detector readout noise	σ_{read}	10	e^-

In contrast, for the model case with a Ca content of 0.1 wt%, the emission-line radiance became much lower even within the range where plasma could be generated, resulting in substantial differences in SNR among the emission lines. Among the three lines evaluated, Ca II 370.74 nm had the lowest SNR, whereas Ca II 393.49 nm had the highest. These differences arose from differences in the absolute line radiance and the plasma-continuum radiance at each wavelength. For low Ca contents, accumulation over multiple laser shots is effective for improving the SNR.

Figure 5(b) shows the single-shot SNR as a function of laser pulse energy and spacecraft-to-target distance for Ca II 370.74 nm at a Ca content of 0.1 wt%. Under the optical-system conditions assumed in this analysis, laser pulse energies ranging from several hundred millijoules to several joules were required to reach the plasma formation threshold at kilometer-scale distances. Therefore, extending the observation range of LIBS from orbit requires not only sufficient laser pulse energy but also a larger telescope aperture, improved laser beam quality, and a higher Strehl ratio to deliver sufficient laser fluence to the target surface. Optimizing the laser wavelength and pulse width to reduce the plasma formation threshold of the target material may also be effective.

Figure 6 shows the fractional contributions of each noise source to the total noise variance at the larger-distance detection limit, defined by a single-shot SNR of 3, for 0.1 wt% Ca and a laser pulse energy of 1 J. Although each bar corresponds to a different target distance, shot noise from the plasma continuum was the dominant noise source for all three emission lines. Its contribution was approximately 97.9%, 75.1%, and 93.5% for Ca II 370.74 nm, Ca II 393.49 nm, and Ca I 422.80 nm, respectively. For Ca II 393.49 nm, shot noise from reflected sunlight also accounted for approximately 20.5% of the total noise variance. The contributions from shot noise from the emission line and detector readout noise were small compared with these background components.

Shot noise from the plasma continuum became dominant in the low-Ca-abundance case primarily because only the Ca emission-line radiance was scaled from approximately 39.9 wt% in HAp to 0.1 wt%, corresponding to a reduction by a factor of about 399, while the plasma continuum was assumed to remain unchanged. In addition, Ca II 370.74 nm had a lower line-to-continuum ratio than the other representative lines even in the HAp measurements, making the relative contribution of the continuum particularly large when extrapolated to low Ca abundance. These results indicate that improving the detection of low-abundance elements requires not only reducing detector readout noise but also suppressing the contribution of the plasma continuum through measures such as optimization of time gating and the spectral bandwidth.

However, the assumptions of linear scaling of the Ca emission-line radiance with Ca abundance and an unchanged plasma continuum have not been validated using samples with different Ca contents. The actual plasma continuum is expected to depend on factors such as the composition of the target material, the amount of ablated material, electron temperature, and electron density. Future experiments using samples with different Ca contents are therefore needed to evaluate the relationship between emission-line radiance and Ca abundance, as well as the dependence of the continuum emission on target composition and its temporal evolution.

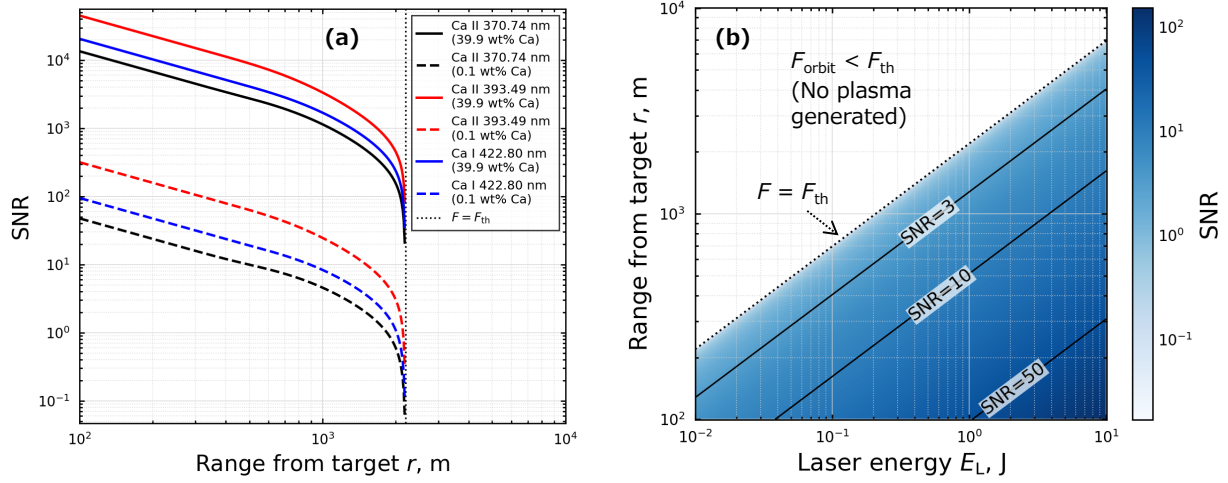


Figure 5. Single-shot LIBS detectability from orbit: (a) SNR as a function of range for the three representative Ca emission lines at a laser pulse energy of 1 J and (b) SNR as a function of laser pulse energy and range for Ca II 370.74 nm at a Ca abundance of 0.1 wt%.

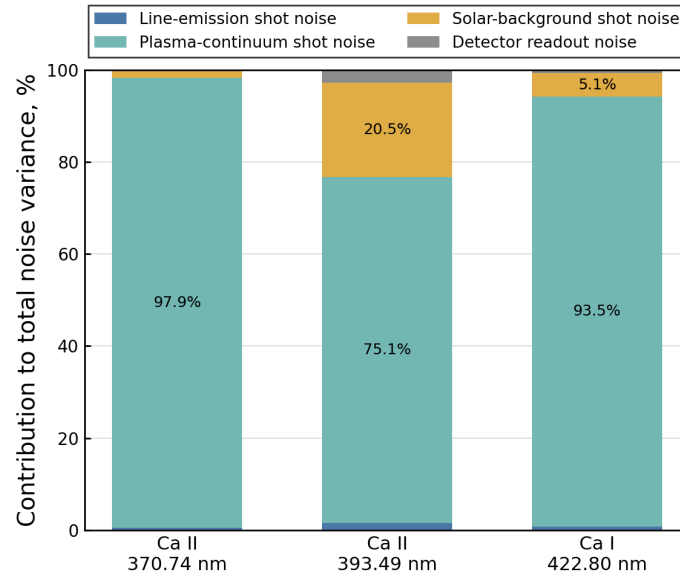


Figure 6. Contributions to the total noise variance at the single-shot detection criterion of SNR = 3.

4. CONCLUSIONS

In this study, LIBS experiments under vacuum conditions using HAP, together with a model for orbital observations, were used to evaluate the feasibility of elemental detection on airless planetary surfaces using LIBS from orbit. Absolute radiometric calibration was applied to the Ca I and Ca II emission spectra measured under vacuum conditions, and the emission-line and continuum components were quantified by estimating the plasma continuum and fitting the emission lines with Voigt profiles. Their dependence on laser fluence was then represented using the model developed in this study, which incorporates a plasma formation threshold, and the single-shot SNR was evaluated by considering the emission-line signal, plasma continuum, reflected sunlight, and detector readout noise under orbital observation conditions.

The analysis showed that, for the high-Ca-abundance case, the maximum observation range was primarily limited by the plasma formation threshold at the target surface, and the results indicated the feasibility of detection at kilometer-scale distances under the assumed transmit and receive conditions. For the 0.1 wt% Ca case, in which the Ca emission-line radiance was assumed to scale linearly with Ca abundance, shot noise from the plasma continuum was the dominant noise source near the detection limit, and the detection performance strongly depended on the line-to-continuum ratio of each emission line. For the detection of such low-abundance elements, accumulating signals from multiple laser shots is expected to improve the SNR and may extend the detection range.

Future work should include LIBS experiments under vacuum conditions using simulants representative of the rocky compositions of asteroids and other planetary bodies, and evaluation of the emission characteristics of a wider range of elements in addition to Ca, to establish a quantitative method for evaluating LIBS observations from orbit. Systematic evaluation of the effects of laser wavelength and pulse width on the plasma formation threshold and emission-line characteristics is particularly important for determining the required laser pulse energy and achievable detection range. In parallel with these experimental studies, the transmit and receive system should be further investigated, including the telescope aperture, laser beam quality, Strehl ratio, receiver field of view, optical transmission, and detector characteristics, to comprehensively evaluate the feasibility of a LIBS observation system from orbit.

REFERENCES

- [1] Maurice, S., Clegg, S. M., Wiens, R. C., et al., "ChemCam activities and discoveries during the nominal mission of the Mars Science Laboratory in Gale crater, Mars," *Journal of Analytical Atomic Spectrometry* 31(4), 863-889 (16 February 2016). <http://dx.doi.org/10.1039/C5JA00417A>
- [2] Maurice, S., Wiens, R. C., Bernardi, P., et al., "The SuperCam Instrument Suite on the Mars 2020 Rover: Science Objectives and Mast-Unit Description," *Space Science Reviews* 217(3), Article 47 (12 April 2021). <http://dx.doi.org/10.1007/s11214-021-00807-w>
- [3] Sridhar, R. V. L. N., Goswami, A., Lohar, K. A., Malathi, S., and Sriram, K. V., "Chandrayaan-3 LIBS Sensor: Preflight Characterization, Inflight Operations, and Preliminary Observations," *IEEE Sensors Journal* 25(2), 2554-2566 (15 January 2025). <http://dx.doi.org/10.1109/JSEN.2024.3506037>
- [4] Sallé, B., Lacour, J.-L., Vors, E., Fichet, P., Maurice, S., Cremers, D. A., and Wiens, R. C., "Laser-Induced Breakdown Spectroscopy for Mars surface analysis: capabilities at stand-off distances and detection of chlorine and sulfur elements," *Spectrochimica Acta Part B: Atomic Spectroscopy* 59(9), 1413-1422 (20 September 2004). <http://dx.doi.org/10.1016/j.sab.2004.06.006>
- [5] Maurice, S., Wiens, R. C., Saccoccio, M., et al., "The ChemCam Instrument Suite on the Mars Science Laboratory (MSL) Rover: Science Objectives and Mast Unit Description," *Space Science Reviews* 170(1-4), 95-166 (14 July 2012). <http://dx.doi.org/10.1007/s11214-012-9912-2>
- [6] Chang, H., Jin, X. and Zhou, W., "Experimental investigation of plume expansion dynamics of nanosecond laser ablated Al with small incident angle," *Optik* 125(12), 2923-2926 (June 2014). <http://dx.doi.org/10.1016/j.ijleo.2013.12.083>
- [7] Nakamura, Y., Moriyama, D., Isomura, A. and Sasoh, A., "Measurement of ablation impulse and direction with oblique laser-pulse irradiation," *Acta Astronautica* 207, 193-199 (June 2023). <http://dx.doi.org/10.1016/j.actaastro.2023.03.017>
- [8] Liland, K. H., "4S Peak Filling - baseline estimation by iterative mean suppression," *MethodsX* 2, 135-140 (2015). <http://dx.doi.org/10.1016/j.mex.2015.02.009>