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Evidence of feasible hardness test on Mars using ratio of ionic/neutral emission intensities measured with laser-induced breakdown spectroscopy in low pressure CO_2 ambient gas

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An experimental study is conducted on the possibility and viability of performing hardness measurement of the various stone and chert samples in low pressure (600 Pa) CO_2 ambient gas, a condition that is encountered in the Mars atmosphere. For this study, a nanosecond Nd-YAG laser is employed to generate plasma emission from the samples with different degrees of hardness. This technique is developed in light of the role of the shock wave in the generation of a laser-induced plasma. It was previously shown that the speed of the shock front depends on the hardness of the sample, and a positive relationship was found between the speed of the shock front and the ionization rate of the ablated atoms. Hence, the ratio of the intensity between the Mg II 279.5 nm and Mg I 285.2 nm emission lines detected from the laser-induced plasma can be used to estimate the hardness of a material. In fact, it is shown that the ratio changes linearly with respect to changes of sample hardness. The result has thus demonstrated the feasibility and viability of using LIBS for non contact hardness measurement on Mars. *Published by AIP Publishing.*
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INTRODUCTION

Taking the unique advantage of the powerful and practical technique of laser-induced breakdown spectroscopy (LIBS) for spectrochemical analysis,[1–8] the LIBS instrument for extraterrestrial applications has been installed for the first time onboard the NASA Mars Science Laboratory (MSL) Rover "Curiosity" launched in 2011. A large amount of data collected *in situ* beamed back to earth bound station for further analysis have since provided researchers with valuable information on the chemical compositions of rocks, soil, and pebble in areas covered by the Rover, including depth profiles of rock weathering layers.[9–17]

Apart from those data, data on the hardness of the geological materials will provide useful additional information for the study of geological formation processes. The acquisition of such data using conventional technique has so far relied on the limited samples brought back from Mars on the return voyage of the space vehicle. Unfortunately, the successful application of LIBS for *in situ* spectrochemical analysis in the low pressure CO_2 ambient gas on Mars has yet to catch the researchers attention of its potential application for hardness measurement.

Our previous study[18] of nanosecond Nd-YAG laser induced plasma emission characteristics in low pressure CO_2 ambient gas has demonstrated its viability for spectrochemical application on Mars. The time resolved spectroscopic measurement performed in that study revealed the dynamical emission characteristics which confirmed the shock wave excitation mechanism in the shock wave driven plasma expansion process in CO_2 ambient gas. When irradiated with a relatively low laser power density, the particles initially ablated from the target are mostly in the form of neutral atoms, and ionization of the ablated atoms takes place behind the shock front developed during the plasma expansion process. The ionization process is intensified as the plasma

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expansion speed increases, leading to the formation of shock wave with the highest temperature generated just behind the shock front, as predicted by the Rankine–Hugoniot equation.[19] This increased ionic emission may eventually dominate over the intensity of neutral atoms depending on the shock wave plasma speed attained in the process. The stronger repulsive force from a hard target is expected to give rise to a higher plasma expansion speed, resulting in higher ionic emission intensity. This phenomenon is frequently observed for elements having low ionization energies, such as Ca and Mg. It was demonstrated in our previous work[20] that the Ca ionic emission intensity from a hard stone sample is much stronger than the corresponding neutral emission intensity, and the reverse is true for a soft sample containing Ca, due to the lower plasma expansion speed as a consequence of weak repulsive force provided by the soft target. Therefore, the ratio between the Ca emission intensities of the ionic line and neutral line may be used to estimate the sample hardness. This experiment is aimed to examine and demonstrate the feasibility of measuring sample hardness using LIBS, according to the simple idea explained earlier in low pressure (600 Pa) CO_2 ambient gas for *in situ* application on Mars. It is important to recall that previously reported works on hardness measurement with LIBS were performed with ambient air.[20] The emission lines chosen for this study are the neutral Mg I 285.2 nm and ionic Mg II 279.5 nm emission lines of Mg which is commonly found in geological objects. The use of Mg emission lines instead of Ca emission lines used in our previous work[20] is due to the fact that the high resolution spectrograph used in this experiment has a narrow wavelength range of single measurement (18 nm) which is just enough to accomodate both Mg emission lines in a single aquisition (285.2 nm – 279.5 nm = 5.7 nm) whereas this was not enough for both Ca emission lines (422.6 nm – 396.8 nm = 22.8 nm).

EXPERIMENTAL PROCEDURE

The schematic diagram of the experimental arrangement is given in Fig. 1. In this experiment, the ns 1064 nm Nd:YAG (Quanta Ray, LAB 130-10, 8 ns maximum energy of 450 mJ) is operated in a Q switched mode at a repetition rate of 10 Hz with fixed output energy of 40 mJ. The laser beam is focused by a multilayer lens (f = 120 mm) through a quartz window of the sample chamber onto the sample surface. The shot to shot fluctuation of the laser is estimated to be approximately 3%. The samples investigated are a variety of stones and cherts with different hardnesses which are known to contain Mg element in their compositions. The sample is placed in a small, vacuum tight metal chamber measuring 11 cm × 11 cm x 12.5 cm, which is evacuated with a vacuum pump and thereafter filled with the CO_2 gas. The CO_2 gas used in this experiment is prepared by Air Liquid with 5N purity and the gas flow through the chamber is regulated to keep the gas pressure at 600 Pa by a needle valve in the airline and another valve in the pumping line. The chamber pressure is measured and monitored with the use of a digital absolute vacuum meter. In this setup, the whole chamber together with the multilayer lens can be moved in the laser beam direction with a stepper motor, or moved stepwise with a micrometer in a direction perpendicular to the laser beam. Depending on the experimental need, the sample can be either rotated at 1 rpm or fixed at a certain position during the irradiation.

The spectral measurement of the plasma emission is carried out by using an optical multichannel analyzer (OMA

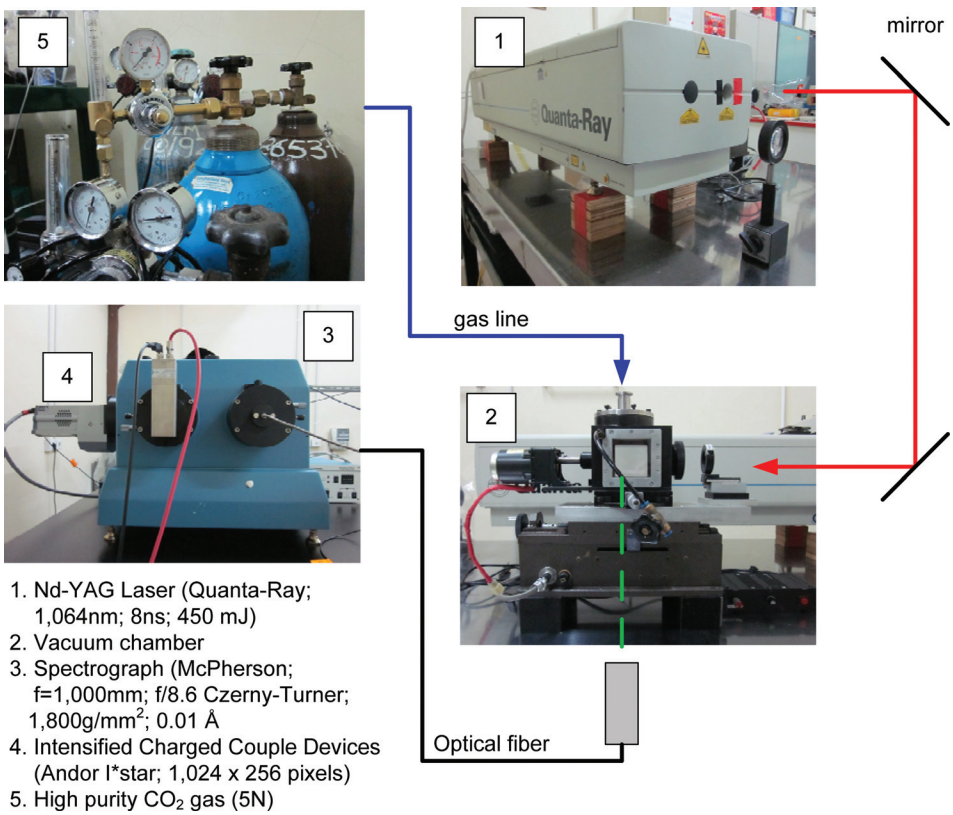

FIG. 1. Schematic diagram of the experimental setup.

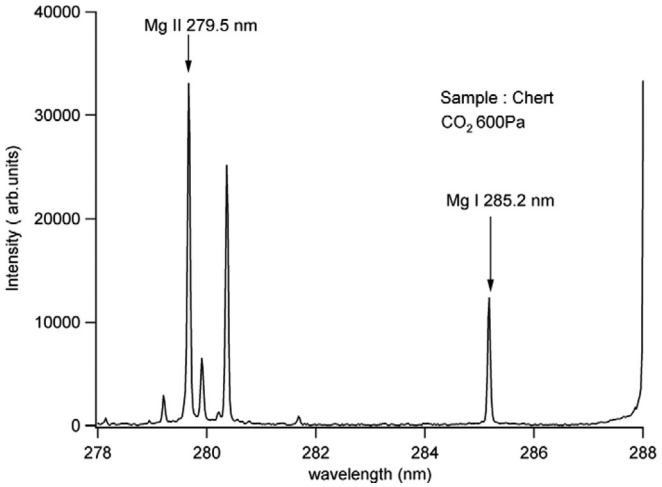

FIG. 2. Space and time integrated emission spectra of chert sample irradiated by 40 mJ Nd-YAG laser at 600 Pa CO_2 ambient gas. The gate delay and gate width of the OMA system are set at 500 ns and 50 μs, respectively.

system, Andor I*Star intensified CCD 1024 × 256 pixels) of 0.012 nm spectral resolution at 500 nm. It is attached to one side of the spectrograph which is connected with an optical fiber on the input port (McPherson model 2061 with 1000 mm focal length f/8.6 Czerny Turner configuration). The entrance end of the fiber is inserted through a cylindrical quartz tube well into the chamber and kept at a position 25 mm sidewise from the sample at various distances from the sample surface. At these positions, the fiber is supposed to collect the emitted radiation entering within 27° of solid angle. The spectral window of the detector has a width of 16 nm at 500 nm wavelength. The accumulated data of 10 successively detected spectra from each irradiated spot are monitored on a screen, and recorded to yield the averaged results presented in this report.

EXPERIMENTAL RESULTS AND DISCUSSION

The time integrated spectrum obtained from a chert sample with gate delay and gate width of 500 ns and 50 μs, respectively, is presented in Fig. 2 which shows the emission lines of Mg II 279.5 nm and Mg I 285.2 nm with certain intensity ratio of Mg II/Mg I of 2.8. However, in view of the generally dynamical nature of the emission intensity, the ratio is expected to vary with time and may offer the most favorable time for its measurement. It is therefore necessary to perform the measurement of time resolved spatially integrated emission intensity of those two Mg emission lines. The result is presented in Fig. 3 along with the time dependent intensity ratio of Mg II 279.5 nm/Mg I 285.2 nm. It is seen that the ionic Mg emission intensity decreases rapidly from its high initial value and becomes hardly observable beyond 4 μs. Meanwhile the generally much lower Mg I 285.2 nm emission intensity only decreases slightly over the same time span. This result suggests that the hardness measurement should be conducted at around 1 μs after the plasma initiation. The detection at this time delay averaged over 10 laser shots on the same spot is found to give the intensity ratio of 4.6. Repeating the same experiment for a softer black stone sample yields the result presented in

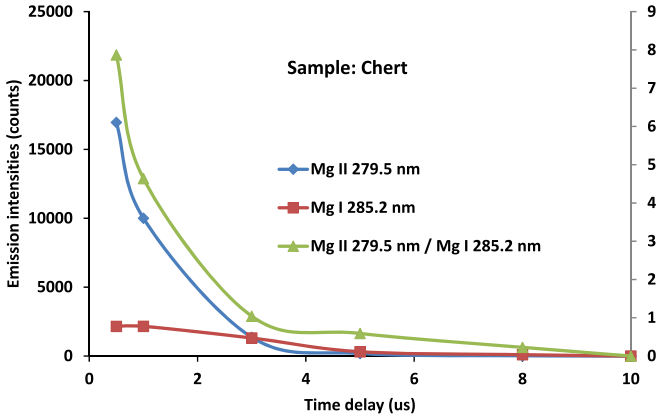

FIG. 3. Time resolved emission intensities of Mg II 279.5 nm and Mg I 285.2 nm along with the Mg II 279.5 nm/Mg I 285.2 nm intensity ratio obtained using chert sample irradiated by 40 mJ Nd-YAG laser at 600 Pa CO_2 ambient gas. The gate width of the OMA system is set at 500 ns.

Fig. 4. It shows exactly the same pattern of time dependent intensity variations for the two Mg emission lines, but the intensity ratio detected at about the same time has a lower value of 3.16. This result amply supports our suggested possibility of using LIBS for estimating the sample hardness.

The ratios cited above are the averages over 10 laser shots. Nevertheless the values appear to grow with increased number of irradiation, suggesting the possible modification of the sample surface properties due to repeated laser irradiation. It is therefore necessary to examine this trend of increasing intensity ratio which may either saturate or undergo a reversal and thereby exhibits the most favorable number of laser irradiation for the determination of the intensity ratio. For that purpose, a series of repeated measurement is performed on the same samples with a fixed OMA delay time of 1 μs and gate width of 1 μs, but various number of laser shots. The resulted variation of the average intensity ratio with respect to increasing number of laser shots on a fixed sample position is presented in Fig. 5 for the same sample. As expected, the trend of increasing intensity ratio does reveal its maximum value or a reversal point between 25 and 30 shots. This number is therefore adopted in the following measurements.

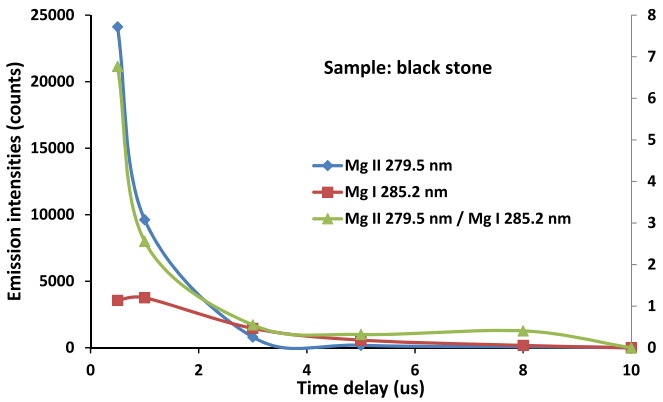

FIG. 4. Time resolved emission intensities of Mg II 279.5 nm and Mg I 285.2 nm along with the Mg II 279.5 nm/Mg I 285.2 nm intensity ratio obtained from black stone sample irradiated by 40 mJ Nd-YAG laser at 600 Pa CO_2 ambient gas. The gate width of the OMA system is set at 500 ns.

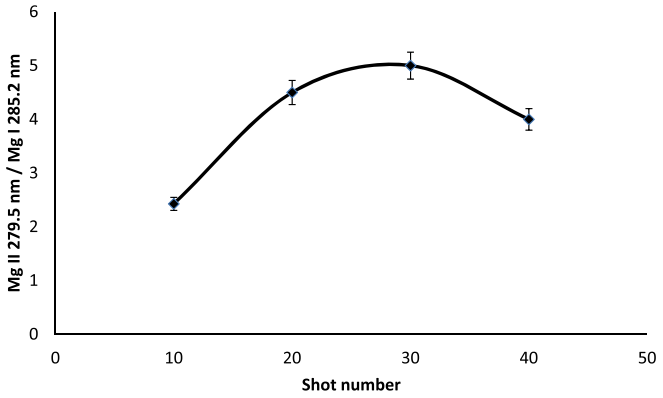

FIG. 5. Ratio of Mg II 279.5 nm/Mg I 285.2 nm emission intensities of chert sample plotted as a function of number of laser shots irradiation on a fixed position of the sample surface. The sample is irradiated by 40 mJ Nd-YAG laser at 600 Pa CO_2 ambient gas. The gate delay and gate width of the OMA system are set both at 1 μs.

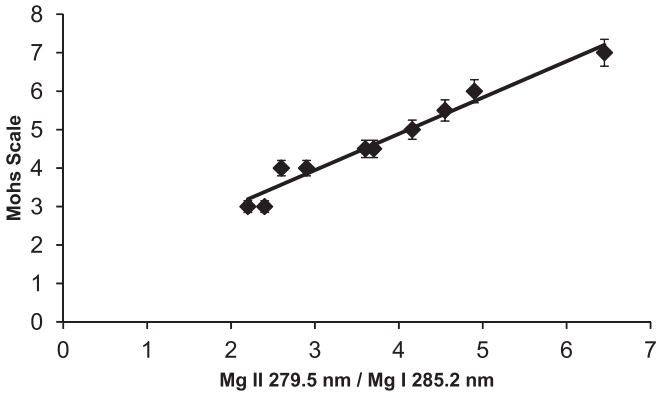

FIG. 7. Relationship between Mg II 279.5 nm/Mg I 285.2 nm intensity ratios and corresponding Mohs scale using different kinds of samples with various hardnesses. Each sample is irradiated by 40 mJ Nd-YAG laser at 600 Pa CO_2 ambient gas. The gate delay and gate width of the OMA system are set both at 1 μs. Data are taken between 25 and 35 laser shots irradiation in fixed condition.

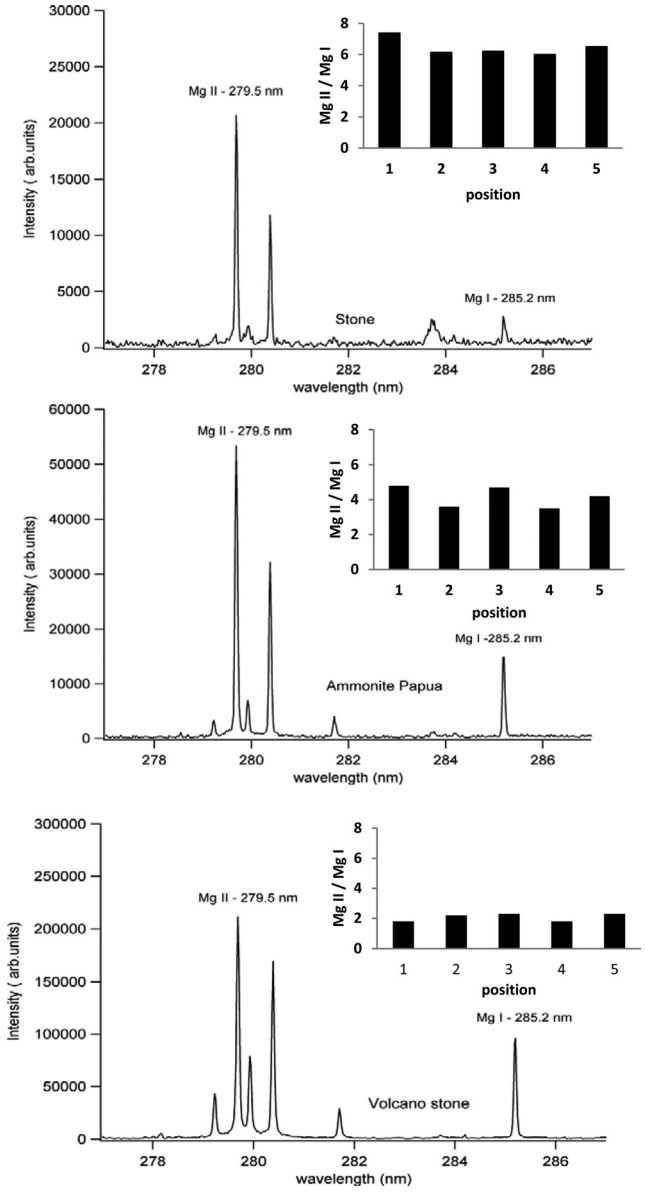

FIG. 6. Emission spectra of (a) stone, (b) ammonite Papua, and (c) volcano stone. Fluctuations of the ratios between Mg II 279.5 nm/Mg I 285.2 nm emission intensities are shown in inset of the corresponding figure.

In order to further testify the applicability of this technique, 3 samples with large differences of hardness are used namely, the stone, ammonite fossil from Papua, and volcano stone. Presented in Fig. 6 are the data obtained from irradiating 5 different spots on each sample. One notices that fluctuations of the measured results shown in the inset are generally small. This figure shows that the hardest stone sample has the highest ratio of Mg II 279.5 nm/Mg I 285.2 nm. Encouraged with this result, various samples with known Mohs scale hardnesses are measured, and the relationship between the ratio of Mg II 279.5 nm/Mg I 285.2 nm against Mohs scale is plotted in Fig. 7. The resulted plot exhibits a remarkable linear relationship demonstrating the feasibility of using LIBS for non contact hardness measurement on Mars.

CONCLUSION

The results of this experiment show the feasibility of measuring the relative emission intensities of the neutral and ionic lines from a certain element (Mg or Ca) ablated from the sample in LIBS for hardness measurement. It is further demonstrated that the space integrated intensity ratio of the two emission lines measured at the early plasma emission and averaged over a certain number of laser shots (25–30) produced a linear calibration line promising for sample hardness estimation.

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