



The feasibility of TEA CO₂ laser-induced plasma for spectrochemical analysis of geological samples in simulated Martian conditions



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ABSTRACT

The present work studies the possibility of using pulsed Transversely Excited Atmospheric (TEA) carbon dioxide laser as an energy source for laser-induced breakdown spectroscopy (LIBS) analysis of rocks under simulated Martian atmospheric conditions. Irradiation of a basaltic rock sample with the laser intensity of 56 MW cm⁻², in carbon-dioxide gas at a pressure of 9 mbar, created target plasma with favorable conditions for excitation of all elements usually found in geological samples. Detection limits of minor constituents (Ba, Cr, Cu, Mn, Ni, Sr, V, and Zr) were in the 3 ppm–30 ppm range depending on the element. The precision varied between 5% and 25% for concentration levels of 1% to 10 ppm, respectively. Generally, the proposed relatively simple TEA CO₂ laser-LIBS system provides good sensitivity for geological studies under reduced CO₂ pressure.

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1. Introduction

Due to its unique characteristics laser-induced breakdown spectroscopy (LIBS) has been developed as a versatile technique for elemental analysis of almost any type of material. LIBS has been successfully applied for chemical analyses of rocks, metals, powders, hazardous materials, liquids, biological materials, etc. ([1] and references therein). It has also been used in demanding environments, such as inside nuclear reactors, on the sea floor, planet Mars, etc.

The first LIBS instrument ever used on another planet is the ChemCam instrument package fitted on the NASA Mars Science Laboratory (MSL) rover Curiosity [2–4]. The primary objective is to determine the composition of geological material and thus obtain knowledge about rock types, their origin and possibly about a genesis and evolution of the whole planet [5]. To date, ChemCam has identified a broad list of elements on Mars, including major elements (Si, Al, K, Na, Ca, Mg, Fe, Ti) [6], minor and trace elements (Li, Mn, Cr, Sr, Rb, Ba) [7], as well as volatiles and halogens (O, S, P, H, Cl, and F) [8–10].

The bases for this achievement were laboratory studies of the performance of LIBS for elemental analysis of geological materials under simulated Martian environmental conditions. ChemCam is equipped with a Q-switched diode-pumped solid-state 1067 nm Nd:KGW laser operating from 3 Hz to 10 Hz, with 5 ns pulses at 30 mJ/pulse (~14 mJ/pulse

on the target) [2,3]. However, most of the laboratory investigations were done using Nd:YAG lasers [11–15].

The Q-switched Nd:YAG laser operating at 1064 nm has been the most widely used laser for LIBS applications. However, high precision and sensitivity were also obtained using TEA CO₂ laser based LIBS for the analysis of a certain type of samples [16,17]. Pulsed TEA CO₂ laser is known as an efficient laser system [18], emitting radiation at 10.6 μm with an output peak power typically in the order of megawatts. When focused, the radiation intensity reaches tens of megawatts per cm², which is usually sufficient for plasma initiation. Compared to the Nd:YAG laser, the TEA CO₂ laser has lower photon energy (approx. 0.12 eV, compared to Nd:YAG of approx. 1.17 eV). TEA CO₂ laser also has much longer pulse duration. The laser-optical pulse has a gain-switched spike, followed by a slowly decaying tail. The full width at half-maximum (FWHM) of the spike is about 100 ns, and the tail about 2 μs. These characteristics may have certain advantages for LIBS application. For instance, compared to lasers with higher photon energy, it is more suitable for optical spectroscopy since the detectors usually have low sensitivity to the scattered TEA CO₂ radiation wavelengths. Further, the *inverse Bremsstrahlung* (IB) process is much stronger in the case of TEA CO₂ laser than the Nd:YAG laser, because plasma absorption coefficient is proportional to the square of the laser wavelength [19]. In the case of TEA CO₂ laser induced plasma, the initial plasma absorbs the remaining laser pulse energy through IB, producing laser heating of the plasma in low density regions far from the target surface. Consequently, spatial discrimination between line and continuum

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emission is improved, and line broadening reduced. Our recent results [20] have shown that when plasma was induced by TEA CO₂ laser irradiation of a copper target, under reduced air pressure, the plasma emission was strong for a relatively long period of time, and the propagation length was relatively large (15 mm) allowing well-resolved narrow spectral lines to be obtained without the use of time-gated detection. It was also found that TEA CO₂ laser is well suited to soil sampling. Because of the high absorbance of soil samples at the wavelength of the TEA CO₂ laser, the plasma can be initiated more easily and the sample blowing-off is significantly suppressed due to the far lower power density and the longer pulse duration as compared to Nd:YAG lasers [16].

A well-established fact is that LIBS spectra greatly depend on composition and pressure of the surrounding gas atmosphere [21,22]. Although LIBS is usually performed in ambient air and at ambient pressure, the use of other gases and pressures offers the possibility to improve the resolution, signal intensity or signal-to-noise ratio (SNR) of LIBS spectra. Interest in non-standard atmospheric conditions is also driven by applications for space exploration. For instance, it has been shown that compared to air, low pressure CO₂ gas has some advantages for LIBS [14,23]. Salle et al. [14] compared LIBS of soil in air at atmospheric pressures and at 7 Torr CO₂. They found that LIBS spectra exhibited improved resolution and an increase in signal-to-noise ratio in a 7 Torr CO₂ atmosphere. In another study involving Mars atmosphere simulation, Brennetot et al. [23] found that LIBS of basalt sample at 7 Torr CO₂ resulted in an improvement when compared with atmospheric conditions. Also, it was shown that the Mars environment favors plasma expansion and lifetime.

In view of the previous facts, the primary objective of this work was to examine the possibilities of using TEA CO₂ laser based LIBS for the analysis of geologic samples under simulated Martian atmospheric conditions. To that end time-integrated space-resolved laser induced plasma spectroscopy (TISR-LIPS) was applied [20,24,25]. A typical volcanic rock (basaltic rock) was chosen as the sample material for this study.

2. Experimental

2.1. Sample preparation and characterization

The rock sample used in the present work was a Tertiary basaltic rock from the Balkan Peninsula, classified according to the TAS scheme as basaltic trachyandesite [26]. A dark gray-colored near hexagonal-shaped sample was prepared by cutting the original natural basaltic rock. The sample was about 35 mm long and ~5 mm thick (Fig. 1). After cutting, the sample surface was processed with grinding paper

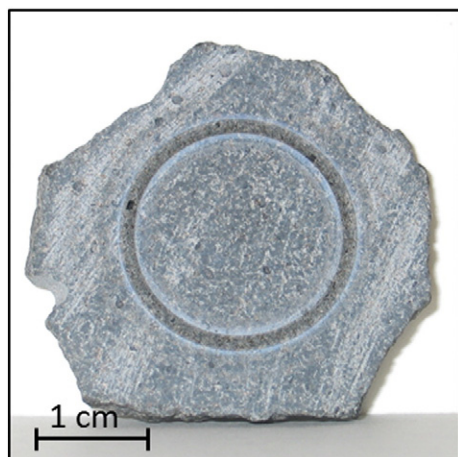


Fig. 1. Photo of the rock sample after laser irradiation – the ring marks the ablated area.

(quality 400) then ultrasonically cleaned, dried in hot air, and kept in desiccator. Just before irradiation, the target was carefully cleaned with ethanol. Elemental composition of the sample is given in Table 1.

The sample surface morphology prior to laser irradiation is shown in Fig. 2a–c. With respect to the typical grain sizes (<1 mm) the sample belongs to a fine-grained rock group [27,28]. The dimensions of a focused laser spot (Fig. 2d) were ~1 mm × ~1 mm (~0.01 cm²), well above the grain sizes of the rock sample. Because of that, the influence of grain size on accuracy and precision of the LIBS analyses is not expected to be large [27]. In addition, each LIBS spectrum is an average spectrum, obtained by accumulation of consecutive spectra from 30 different locations on the sample. For all the lines measured the accumulated spectra had averaged peak intensities with an RSD < 15%, probably as a result of the combination of fluctuations due to laser energy and high degree of surface roughness.

2.2. LIBS setup

The experimental setup is given in Fig. 3. The laser was a TEA CO₂ laser system developed at the VINCA Institute [29]. It is a miniature, compact system. Output characteristics are given in Table 2.

The TEA CO₂ laser pulse had a gain switched peak, followed by a slowly decaying tail (Fig. 4). Full width at half maximum (FWHM) of the peak was about 100 ns, and the tail about 2 μs. The initial spike contained approximately 35% of the total laser energy. Typical output pulse energy was 160 mJ, and the repetition rate 1 Hz. The laser was run in a multimode regime. Unfocused laser beam has a 10 mm × 10 mm square cross-section.

The rock sample was placed in a glass vacuum chamber of ~500 cm³ total volume. The chamber was closed with a NaCl window, CaF₂ windows and Al-plate. The position of the ZnSe lens (focal length of 13.0 cm) was adjustable within ±1.5 cm from the focus. The target was placed at the focus (focused laser spot 1 mm²) with a maximum fluence (Φ) of ~16 J cm⁻² and intensity (I) of 56 MW cm⁻². The sample typically rotated with speed of 0.5 rpm, ensuring always a “fresh” area at the target surface between two successive laser pulses. The chamber was connected to a vacuum and gas handling system. Prior to experiments the gas chamber was evacuated to a rough vacuum and then backfilled with CO₂ gas to the desired pressure. Experiments were conducted in a flowing regime, with the gas flow-rate and pressure regulated with high-precision valves. The operational carbon dioxide pressure in the course of experiments was constant, typically 9 mbar, while the temperature was kept at +15 °C.

It should be mentioned that the term “Martian conditions” refer to 9 mbar of CO₂ gas. Martian atmosphere actually consists of CO₂

Table 1
Composition analyses of basaltic rock obtained using ICP-OES.

	Concentration ^a wt.%		Concentration ppm (μg/g)
SiO ₂	53	Cr	300
TiO ₂	1.1	Ni	100
Al ₂ O ₃	12.2	Co	60
Fe ₂ O ₃	5.7	V	120
MnO	0.10	Cu	70
MgO	4.8	Zn	130
CaO	4.8	Ba	2000
Na ₂ O	2.4	Sr	740
K ₂ O	5.7	Zr	160
P ₂ O ₅	1.2	B	127
LOI ^b	8.6		
Total	99.6		

^a The relative expanded standard uncertainty ranged from 1–3%, in 100 ppm concentration range, to 7–15% for the highest measured concentrations;

^b LOI, loss on ignition.

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