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Laser Induced breakdown spectroscopy (LIBS): Application to geological materials

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Laser-induced breakdown spectroscopy (LIBS) is emerging as an analytical tool for investigating geological materials. The unique abilities of this technique proven its potential in the area of geology. Detection of light elements, portability for in-field analysis, spot detection, and no sample preparation are some features that make this technique appropriate for the study of geological materials. The application of the LIBS technique has been tremendously developed in recent years. In this report, results obtained from previous and most recent studies regarding the investigation of geological materials LIBS technique are reviewed. Firstly, we introduce investigations that report the advancement in LIBS instrumentation, its applications, especially in the area of gemology and the extraterrestrial/planetary exploration have been reviewed. Investigation of gemstones by LIBS technique is not widely reviewed in the past as compared to LIBS application in planetary exploration or other geological applications. It is anticipated that for the classification of gemstones samples, huge data set is appropriate and to analyze this data set, multivariate/chemometric methods will be useful. Recent advancement of LIBS instrumentation for the study of meteorites, depth penetration in Martian rocks and its regolith proved the feasibility of LIBS used as robotic vehicles in the Martian environment.

Keywords: LIBS, gemstone, geological samples, extra-terrestrial.

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Introduction

Geological materials, including rocks and minerals, transmit significant information concerning particular geological environments. This information can be beneficial for studies such as determining reservoir description, mineral provenance, prospecting, and geochemical mapping. However, there is an extensive range of geological materials with identical characteristics. Thus, good discrimination of the samples is challenging. Geologist's assessment is needed for geological survey and following laboratory analyses, which can be time-taking, tedious, and complicated. Laser-induced breakdown spectroscopy (LIBS) utilization on geological materials has been projected over the last two decades for rapid analysis. Laser-induced breakdown spectroscopy is an immaculate and reliable technique based on emission spectroscopy. It rapidly analyzes atomic emission from laser-induced plasma generated by the laser-matter interaction. In this spectroscopic technique, short duration (nanosecond, femtosecond or picosecond) pulsed laser beam focused onto the sample (solid, liquid, gas). The sample surface gets vaporized, then atomize and the vapour ionized by this high energy laser pulse. A plasma plum is formed in which atoms and ions are driven to excited states. By emitting specific radiation of underlying electronic states, these atoms jump to lower energy states. The process is called cooling or expansion of plasma (see Fig. 1 for process involved in the plasma formation and Fig. 2 for the interaction of laser with different laser pulse on the solid surface). An optical spectrum related to plasma emission is obtained using a spectrometer [1–3]. Qualitative and quantitative analysis can be performed on the emission spectra. Atomic lines present in the emission spectra give qualitative information about the element present in the sample. Conventional calibration curve methods and calibration-free (CF-LIBS) methods have been used for the quantitative information of materials analyzed [4–8]. Laser-induced breakdown spectroscopy has various applications in several fields, and many more improvements concerning the related instrumentation are still growing. Laser-induced breakdown spectroscopy can be used at the microscale level to detect chemical mapping and for high spatial resolution [9,10]. In a differing approach, LIBS has been used to analyze the surface of Mars [11]. It can be used within the laboratory or in the field analysis, for close-in analysis or at long distance to analyze hazardous materials [12]. Laser-induced breakdown spectroscopy has thus been applied to many more fields. It is difficult to quote a list of applications of LIBS; since the last five years, more than 5000 articles have been published from basic of LIBS to its applications [13]. Laser-induced breakdown spectroscopy becomes so popular in the geological analysis that Harmon et al. introduced a new word, .GEOLIBS. to analyse geological and environmental samples [14]. The unique features of LIBS make it

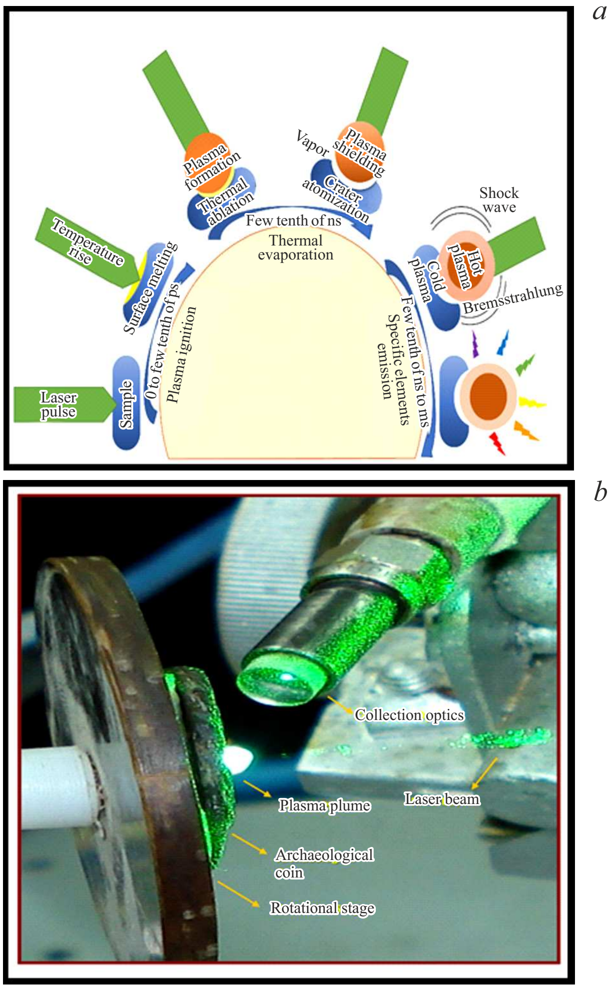

Figure 1. A pictorial view of (*a*) overall processes involved in the laser ablation and the plasma formation on a time scale for a nano-sec laser, (*b*) image of the plasma plume generated by nano-sec laser on the surface of archaeological coins (photograph taken in our Laser Spectroscopy laboratory).

appealing analytical equipment in the vast area of geological materials in field/laboratory/remote analysis. It can detect all the chemical components of solid, liquid and gases with high sensitivity. Laser-induced breakdown spectroscopy is beneficiary over the other spectroscopic technique in detecting light elements (B, Be, C, He, Li, N, and O) available in high abundance in geological materials.

Sample preparation is not necessary for this technique allowing rapid analysis of thousands of samples. Laser-induced breakdown spectroscopy is a spot analytical tool, and it requires a small (few microns) sizes of sample for the analyses without removing the sample from its petrologic context. This allows in-situ, in-field analysis of whole-rock samples [15] or inclusions [16] or chemical mapping of samples [9]. With the help of the LIBS tool, depth profiling of the sample is also possible (see Fig. 2, explaining depth profiling by LIBS) [17,18]. Finally, LIBS is field-portable, extending geochemical analysis into the field; it can also perform remote analysis. It can also readily combine with other techniques, For the molecular analysis with Raman spectroscopy [19] or optical hyperspectral imagery [20]. As a reliable spectroscopic technique, LIBS is growing day by day.

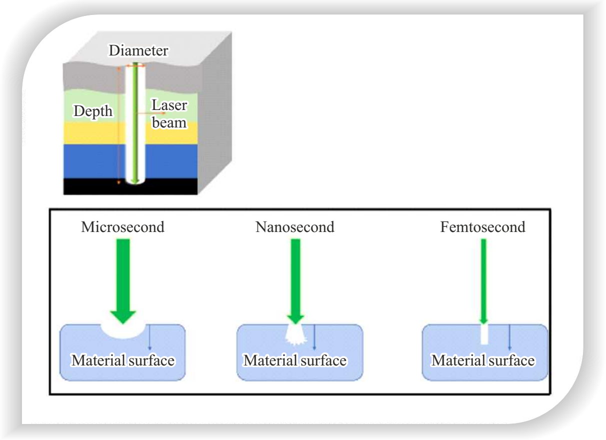

Figure 2. Schematics of dip created by focusing the laser at one point for the study of different layer (up) and the interaction of laser with different pulse width on solid surface (down).

The first geological application of LIBS is by Grant et al. in 1990. Elemental analysis of iron ore is performed using the LIBS technique. After advancement in detectors and lasers, fast acquisition and higher sensitivity have been obtained [21,22]. The first actual geological application was made by Vadillo & Laserna in 1996. They analyzed silicate, vanadate and sulfide rocks by using LIBS [23]. The study of fluid inclusions in minerals is of great interest to geological society. Due to its small laser spot, LIBS demonstrates its potential to access the small (< 30 micrometer) fluid inclusions due to its point detection capability. From 1993 to 2003, many publications reported the use of LIBS prototype for the analysis of fluid inclusions in minerals [24–26]. Quantitative analysis of minerals using LIBS have been performed by many other works [27–30]. Few examples are the concentration of Li in rocks and minerals [15,27], concentrations of major constituents in rocks and meteorites [28], concentrations of heavy elements in oil [29] and moldavite samples from Ries impact structure, Germany [30]. One can consider the planetary or extraterrestrial applications of LIBS, in 1990s LIBS is successfully used in NASA Mars rovers. The application of multivariate statistical techniques to the spectral analysis made it possible to derive more information from each LIBS spectrum, eventually leading to NASA approval of LIBS for the ChemCam instrument on the Mars Science Laboratory and industrial, agricultural, military and geological applications [31].

Furthermore, LIBS, well known for its remote detection feature, was the powerful spectroscopic technique in the ChemCam rover. Many scientists carry out a series of geological studies by analysis of Martian rocks. In this regard, moldavite, an impactite, has been studied using LIBS. The recorded moldavite spectra are expected to aid investigations of planetary analogues, including the study of Martian impact structures having felsic target rocks. Laser-induced breakdown spectroscopy identifies the impact ejected glasses and establishes their internal chemical heterogeneity. The presence of siderophile elements (Cr, Fe, Co, Ni and Mn) in a silica-rich impact indicates the contribution of mafic target materials in creating the moldavite glass or presents from the impactor component [30].

As a consequence of new findings, miniaturization of laser and spectrometer becomes possible, beam optics designs became more compact, and by the use of optical fibres [32], field-portable, handheld, and standoff LIBS has also been developed and applied to numerous studies. For example, backpack type man-portable and mobile LIBS systems have been used for field analysis like museums and factories [33]. The real-time chemical analysis in a cathedral in limestones has been performed using single-pulse standoff LIBS to investigate Ca/Mg and Si/Ca ratios [34]. A backpack LIBS system has been used in a cave to measure Ca, Mg, and Sr concentrations in speleothems [35]. The automated quantitative analysis of bulk minerals and ores have been done by use of LIBS methods [36], continual monitoring of small variations in Si, Ca, Mg, Al, and graphitic C contents in iron-ore [37], on-line analysis of sulfur in Cu and Ni ores, anhydrite, barite, and gypsum, and for on-line analysis of coal ash [38].

The present article reviews the recent advancement in the LIBS technique in the area of geological analysis. The article focuses mainly on the LIBS study of gems and minerals, which is not the much-highlighted topic of review articles. On the other hand, the second focus of this article is a tutorial review of LIBS application in the area of extraterrestrial/planetary analysis, which is the well-discussed topic of review articles.

Instrumentations

Laser-induced breakdown spectroscopy instrumentation is relatively very simple (Fig. 3, *a*). There are many articles related to the instrumentation of LIBS. In 2006 Cramer et al. presented the basic components of LIBS [1]. Thakur et al. (2007) demonstrated instrumentation of LIBS system for a different type of materials [2]. Laser-induced breakdown spectroscopy system consists of four basic units: i) a high energy laser source, ii) a collection optics, iii) a spectrometer, iv) a detector that may be CCD or ICCD. Many laser sources (nanosecond, femtosecond or picosecond) were used in previous works [39,40]. The most popular is a Nd-YAG laser source which can give second and third harmonics (1064 , 532, 266 nm). Many field portable LIBS system consists of Q-switched Nd-YAG laser source working at 1064 nm. Andrade et al. refer to laser as the „heart" of the LIBS system [41]. It generates a high-energy laser pulse with a short pulse duration (typically of few nanoseconds). The generated pulse falls on the sample surface, and as a consequence of high energy few micrograms of sample ablated from the sample. This ablated part of the sample undergoes a few processes, and the plasma is formed. The next laser pulses increase the temperature of the plasma and excite the lower energy level atoms to the higher level. After that, the plasma cools down, and the atoms jump to the lower level and emit energy in the form of photons. To collect these photons, collection optics and fibre cables were used. When the sample is at a distant telescope was used for the collection of photons. The detection system consisting of a spectrometer and the CCD or intensified CCD was used to monitor and record the signals. Cremers and Radziemski (2006), Singh and Thakur (2007) described the various type of spectrograph and CCDs [1,2]. For the field-portable LIBS and handheld LIBS system, compact lasers and more sensitive detection systems were used in recent years. A field-portable LIBS system was developed for rapid, on-line detection, identification, and investigation for geological study [35,42] (Fig. 3, *b–d*). J. Cunat et al. (2005) used a field-portable LIBS system for the characterization of speleothems in karstic caves [35]. Recently, in 2021, Russell et al. have written an invited review that contains the description of the experimental set up for the rapid and real-time analysis of the geological materials [42]. Instrumentation of fp-LIBS and mp-LIBS can be read elsewhere [43]. It seems from the instrumental setup that LIBS is complex, but simplicity is one of the main characteristics of the LIBS system.

Application of LIBS in gemology

As we know, gems are very precious and often used in ornaments/jewellery. The gemology area is very broad, and the reliability of gems is very concerning topic for gemmologists and mineralogists. For the identification and provenance of gems, a spectroscopic tool is needed that should not damage the precious stones. Many spectroscopic techniques (ICPMA, EPMA, XRD, XRF, etc.) and molecular techniques (IR, VNIR, Raman etc.) have been used for analysis purposes. But LIBS became so popular in a very lesser time. Laser-induced breakdown spectroscopy is a quasi-destructive technique as the laser spot is very small, so it has shown high potential for the chemical identification of gems. The provenance of gems is also a high rated analysis area for the mineralogist and petrologist. A single LIBS spectrum can provide all the information needed for the provenance of gems, so LIBS considered as a rugged, cost-effective, and reliable tool for study of gems provenance.

The first article on the provenance of gemstones has been reported by McMillan et al. (2006) [44]. It demonstrates LIBS analysis of 96 beryls from 15 countries (Afghanistan, Brazil, Canada, China, Colombia, India, Ireland, Italy, Madagascar, Mexico, Mozambique, Namibia, Norway, Russia, Tanzania), Antarctica, and ten USA states (AZ, CA, CO, CT, ID, ME, NC, NH, NM and UT). This study shows

Figure 3. Experimental setup of LIBS system: (*a*) a traditional LIBS setup used in the laboratories, (*b*) a standoff LIBS system consisting of a telescope to detect the samples at some distance, (*c*) a field-portable LIBS system, compact in the structure to study the samples in the field, (*d*) a very compact handheld LIBS system for quick analysis of samples.

optimal analysis condition for the beryl, i.e., laser pulse energy of 102 mJ and time delay of 2 us. They found unexpectedly high variability in emission line intensities. The results highlighted the difficulties in the analytical procedure. To compare the samples from various origination, LIBS analysis should be done in the vacuum or Ar atmosphere. Synthetic emeralds grown by different techniques have been analyzed by the LIBS technique [45]. The quantitative study of trace element using the CF-LIBS method and one-point calibration LIBS have been determined and correlated with the origin of synthetic emerald gemstone. It might be a possibility that natural emerald gemstone shows different characteristics from synthetic emerald. Comparative study of natural and synthetic emeralds by LIBS technique will be a good work in this area. Tempesta et al. analyzed six rare samples of red beryl using the CF-LIBS technique and compared the results with Raman spectroscopy and VIS-NIR reflectance spectroscopy results. Laser-induced breakdown spectroscopy identification is in agreement with the molecular analysis. The work confirmed the direct correlation between the concentration of trace element Mn (a chromophore) and the red color saturation of red beryls [46]. Laser-induced breakdown spectroscopy, in conjunction with multivariate analysis, shows a high potential for the problems dealing with gems provenance. Many works used PCA and PLSR statistical methods for the provenance of beryls [47], diamonds [48], and other silicate minerals [49]. As provenance analysis deals with thousands of spectra, it is suitable to use statistical methods. McManus et al. applied PCA to the LIBS spectral data of 39 beryl samples of 11 pegmatite mines in New Hampshire, Connecticut, and Maine (USA). Samples from the different zones have been successfully recognized by LIBS analysis [47]. For the quantitative analysis of thousands of spectra, another multivariate technique PLSR has been used. Kochelek et al.have studied 569 rough sapphire and ruby specimens from 21 localities in 11 countries using laser-induced breakdown spectroscopy. They have demonstrated that the determination of country or deposit of origin may be related to a quantitative measure with a high level of success. They have developed and used a sapphire provenance algorithm and ruby provenance algorithm using LIBS spectral data. For sapphires, the matching algorithm consists of 8 models. The model correctly predicts 98.9% of the country-of-origin validation spectra and 97.9% of the origin deposit validation spectra. For rubies, the matching algorithm consists of 12 models. The model correctly predicts 96.0 percent of the country-of-origin validation spectra and 95.4 percent of the origin deposit validation spectra. Another work uses LIBS accurately (98.3% accuracy) to determine the provenance of diamonds. A new statistical method, bayesian statistics, was applied to more than 2300 LIBS spectra of 300 diamonds in this study. This study demonstrates that the C-C and C$-$N molecular bands are responsible for multivariate analysis rather than elemental signatures [48].

Finally, LIBS with multivariate analysis can be used for the analysis of a large set of samples. Laser-induced breakdown spectroscopy can be used in the gems industry for industrial purpose. Large set of sample online analyzed by LIBS and multivariate analysis without minimal sample destruction. The use of software like Quantagenetics. [50] will be good for the analysis purpose.

Application of LIBS for the extraterrestrial analysis

The word extraterrestrial stands for the materials from outside of the Earth atmosphere. The compatibility of LIBS for the analysis of geological materials has become so popular in few years that it is not just analyzing the material of earth but also applicable beyond the earth. The very first application of LIBS for extraterrestrial analysis was by De Giacomo et al. in 2007 [51]. In this work, the CF-LIBS approach was used to investigate four certified meteorites belonging to different typologies [Dofhar 461 (lunar meteorite), Chondrite L6 (stony meteorite), Dofhar 019 (Mars meteorite) and Sikhote Alin (irony meteorite)]. The concentration of major elements (O, Si, Ti, Mg, Fe, and Ca) and two minor elements (Mn and Cr) were determined. The concentration of Ni, Fe and Co have been determined for the irony meteorite. The work suggests an important source of error is the measurement of O content in the samples. It also suggests that the element/silicon ratio is important because it is not always suitable to determine all the components. The elemental ratio of Fe/Si, Ca/Si, Mg/Si and Mn/Si is calculated for the Lunar, Martian and stony meteorites. In a subsequent analysis by Dell.Aglio et al. (2010) LIBS technique is applied for the identification and classification of meteorites (Dhofar 019, Dhofar 461, Sahara 98222, Toluca, Sikhote Alin and Campo del Cielo) [52]. In this study, the Ar atmosphere has been used to detect the O content in the Martian meteorites. Also, concentration profiles for major elements Fe, Ni, and Co have been detected for iron meteorite Toluca. The Dergaon Meteorite has been studied by Rai et al. (2020). CF-LIBS method has been used to investigate the elemental concentration of lighter elements H, N, O. Along with atomic lines, molecular emissions of FeO has also been observed in this study [53]. Laser-induced breakdown spectroscopy has been developed for robotic vehicles and successfully implemented in planetary exploration from the past few years. These systems are compact, have multi-sensor systems for in situ analysis of minerals and elemental components of planetary rocks and sediments. Implementation of LIBS on the NASA Mars rovers was explored in the 1990s. In the first week of August 2012, NASA.s Curiosity rover landed on Mars. ChemCam science package positioned to the Mars Curiosity rover has been adorned with the LIBS system to explore the geological layers of the Red Planet (Fig. 4) [54]. In this way, this technique is also being used to study the geological layers of Mars. The photograph of Martian rocks (Fig. 4, *e*) appears like sedimentary, distinct layers formed in aqueous environments. The spectral signatures observed from the ChemCam indicate the possibility of water on Mars. The ChemCam identified gypsum, a water-bearing non-metallic calcium sulphate mineral ($CaSO_4 \cdot 2H_2O$), as veins on the rim of Endeavour Crater, Mars as veins [55]. Therefore to know the environment on Mars that is responsible for gypsum, Rai et al. [56] studied gypsums samples from varied terrestrial environments. Textural types have been analyzed for their inter-sample comparison using LIBS data combined with multivariate statistical analysis methods, which can be correlated with the data of ChemCam LIBS sensitivity to the water content, and in particular hydration levels of calcium, sulfates can discern between anhydrite (CaSO4), bassanite, $CaSO_4 \cdot 1/2H_2O$, and gypsum very quickly, and it has demonstrated in the study. The present-day denudation, topography indicted water and wind actions. The arrested loose sand with wind form ripples in the small valley. This type of topography is also seen on earth, where there is an intercalated sequence of sandstones and shales. It seems that Mars also has experienced similar condition to earth. But the big questions are that there was life? The answer doesn't have, and it is still a mystery. Many works have been performed to study the terrestrial materials in Martian conditions [57]. The standoff LIBS study has been done to optimize quantitative analysis. Also, investigation of LIBS performance in variational pressure atmosphere has been done in many works [58]. The multivariate analysis of spectral data of LIBS gives feasibility to investigate multiple spectra simultaneously. This approach is used in many works [59–64]. Three chemometric methods, principal components analysis (PCA), soft independent modeling of class analogy (SIMCA) and partial least-squares discriminant analysis (PLSDA), have been used to investigate the feasibility of Martian rocks for classification using remote LIBS. The study demonstrated that SIMCA is less sensitive than PLSDA but suitable for studying unknown rock [60]. In a subsequential analysis, partial least squares (PLS), multilayer perceptron artificial neural networks (MLP ANNs) and cascade correlation (CC ANNs) were used for the quantification of rock samples. The results show that PLS without averaging was the accurate method and superior to ANNs [61]. Laser-induced breakdown spectroscopy system was developed for the Pasteur instrument payload of the European Space Agency's 2016 ExoMars mission [62]. In another study, LIBS has been used to investigate soils, rocks and ice at subzero temperatures in simulated Martian conditions [63].

Conclusions and future aspects

In the present article, the potential of the LIBS technique has been demonstrated for the analysis of geological samples mainly Gemstone, and extraterrestrial objects. The

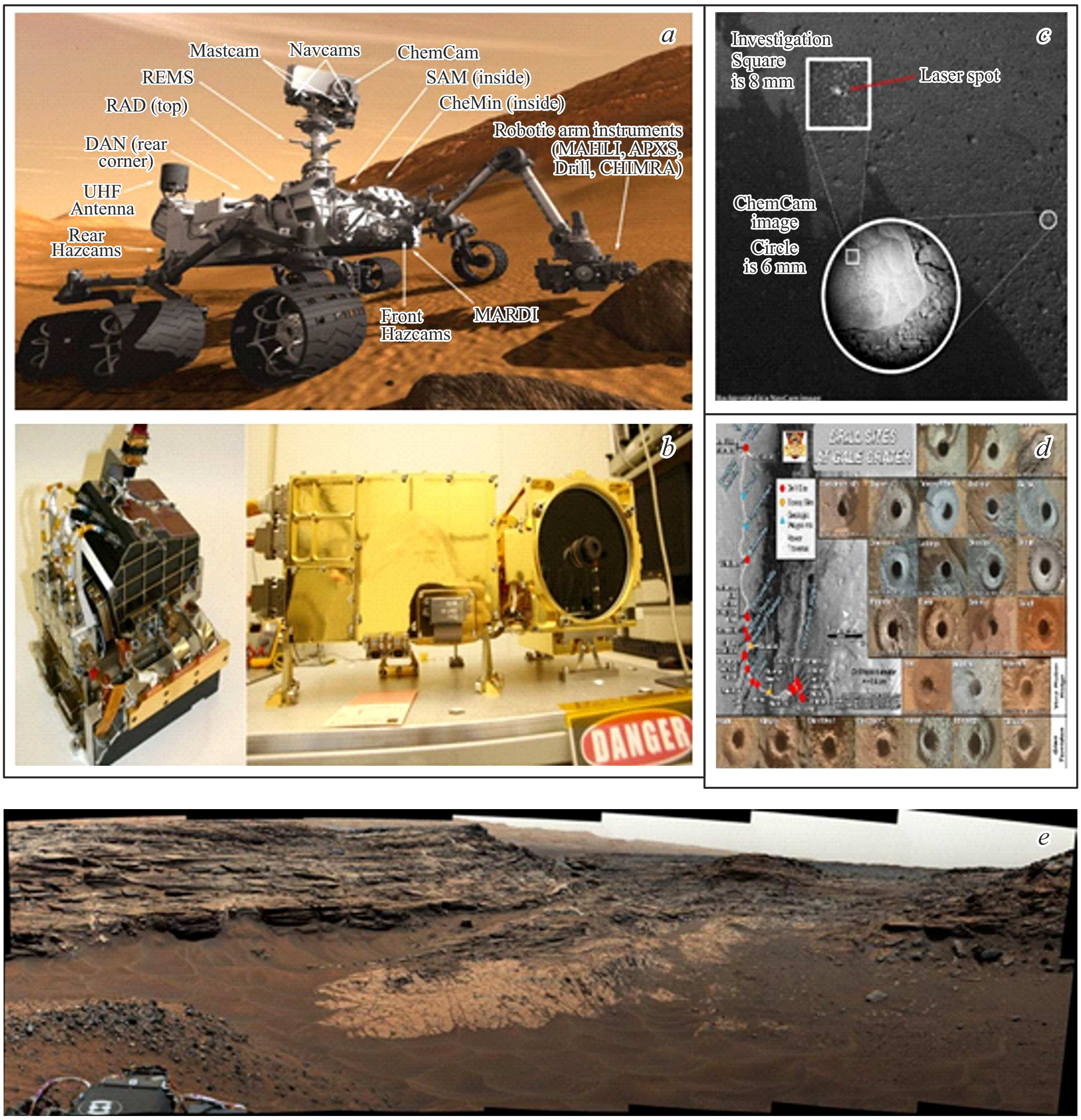

Figure 4. Mars Curiosity rover on the surface of Mars since Aug 2012. (*a*) Various science instruments of Curiosity rover, e.g., cameras, spectrometers, detectors (Courtesy NASA/JPL-Caltech. (*b*) Two main parts of the ChemCam instruments: mast unit (right side) contains ChemCam's laser, imager and telescope; body unit (left side) analyzes the light coming from the telescope (image courtesy NASA/JPL-Caltech/LANL). (*c*) Circle showing the magnified image of rock „Coronation“, it is the first rock on an extraterrestrial planet to be investigated by such laser test, square shows the laser spot (image courtesy NASA/JPL-Caltech/LANL/CNES/IRAP). (*d*) 26 holes drilled by Curiosity rover in different rocks of Gale crater (Courtesy NASA/JPL-Caltech/MSSS). (*e*) Image of „Marias Pass“ area where a geological unit of mudstone (pale zone at center) lies in contact with a geological unit of sandstone (Image courtesy NASA/JPL-Caltech/MSSS).

LIBS process, including plasma formation, collection of emission from plasma, and analysis, has been discussed in great detail. The use of different laser pulse width like a nanosecond, femtosecond for the LIBS and study of gemstone has also been discussed. It is concluded that a shorter laser pulse is more useful for the study of gemstones. The study of the provenance of gemstones has also been discussed. Laser-induced breakdown spectroscopy proved its potential for such study. Since in LIBS very large data is available, multivariate analysis is also helpful here.

Applying multivariate analysis on LIBS data classification of different gemstones was discussed. Using multivariate technique provenance study of gemstones became more reliable. For the quantitative analysis, CF-LIBS and PLSR are the most straightforward approach as there are no references for applying the traditional calibration approach. The application of LIBS for the study of extraterrestrial subjects also has been discussed. A well-known Mars rover Curiosity was equipped with LIBS instrumentation named ChemCam, which shows the usefulness of the LIBS in the elemental analysis.

Thus, the present article explores the usefulness of the LIBS for the elemental analysis of geological terrestrial and extraterrestrial samples. Laser-induced breakdown spectroscopy, along with multivariate analysis, makes it a more robust analytical technique. As LIBS provides only elemental constituents of the samples, which is not more appropriate for studying various samples, it is sometimes more important to know the sample's molecular constituents. In this view, a combined LIBS-RAMAN analysis/ LIBS-LIF analysis will give more detail about the gemstones.

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Author contributions

Ms S. Dubey has the idea for the article, and she prepared the first draft of the manuscript. The manuscript is critically revised by R. Kumar and A.K. Rai. Editing and supervision is done by A.K. Rai.

Conflict of interest

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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