



## LASER INDUCED BREAKDOWN SPECTROSCOPY OF GEOLOGICAL SAMPLES

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### ABSTRACT

*A highly sensitive laser-based spectroscopic technique, the laser induced breakdown spectroscopy (LIBS), for trace element detection has been developed at our laboratory. This method is based on the study of plasma resulting from interaction of intense laser radiation with sample medium. This technique is demonstrated to be able to detect all the significant major and trace elements including Ni, Cu, Mg, Mo, Cr, K, Na, Ca and Fe, present in the rock samples collected from different parts of the Arabian shield. Atomic emission spectra of different trace elements contained in the rock samples have been recorded in the 300 –700 nm region. The 308 nm (XeCl) laser radiation from a Lambda Physik Model EMG 203 excimer laser at an irradiance of  $7.6 \times 10^{10} \text{ W. cm}^{-2}$  has been used. The atomic emission lines were recorded using grating monochromator and detected with photomultiplier. The electrical signal generated by photomultiplier was fed into Box-car averager and processed by signal processor. The observed spectral lines have been assigned to transitions in the neutral charge state of the corresponding atoms of the material under investigation.*

**Keywords:** Laser induced breakdown spectroscopy (LIBS), atomic emission spectrum analysis, rock and mineral analysis, UV laser ablation, microanalysis, remote-sample in situ analysis.

(LIBS)

( - )

(EMG203)

(XeCl)

.  $7.6 \times 10^{10} \text{ w:cm}^{-2}$

(grating monochromatic)

. photomultiplier

## 1. INTRODUCTION

There is growing interest in the development of sensors for rapid and accurate analytical techniques for the chemical species present in the rocks, minerals, waste disposal sites, soil and water samples. More efficient instrumental techniques are now replacing the earlier time-consuming and laborious techniques of wet-chemical analysis. The volume of measurements to be performed today and in future have a prohibitive cost to acquire samples and to take them to a laboratory for analysis. To overcome these huge costs and other logistic problems, new methods are required to perform remote measurements quickly and efficiently. New techniques which are laser based are being developed for remote real time analysis of the minerals, rocks, contaminated liquid and solid samples. Laser induced breakdown spectroscopy is a very sensitive, selective technique for achieving these objectives for in situ measurements [Zhang et. al, 1999, Zolotovitskaya et. al, 1997, Gornushkin et. al, 1997, Barbini et. al, 1999].

LIBS is based on the study of plasma resulting from interaction of intense laser radiation with sample medium. The laser source serves to vaporize, atomize and excite the sample material and the light emitted from plasma is spectrally resolved and analyzed for the identification and concentration of the trace elements present in the sample. LIBS has been applied successfully for the analysis of gases, liquids, solids, solid aerosols, liquid aerosol and soils. Heavy and toxic trace metals such as Cd, Cr, Hg, Pb and Zn can be detected by LIBS in soil and water samples at a ppb-level detection limits remotely.

The unique features of LIBS are: low analysis cost per sample, ability to analyze large number of samples in short amount of time, measurement precision sufficient for screening many elements of interest, high sensitivity and possibility of in situ detection from remotely-located samples. LIBS has been applied in many applications, covering a wide variety of areas of interest such as pollution monitoring (contaminants in liquids, solid and gaseous samples) trace element analysis of soil and water, immediate determination of ore grades during mining and prospecting and industrial chemical process control.

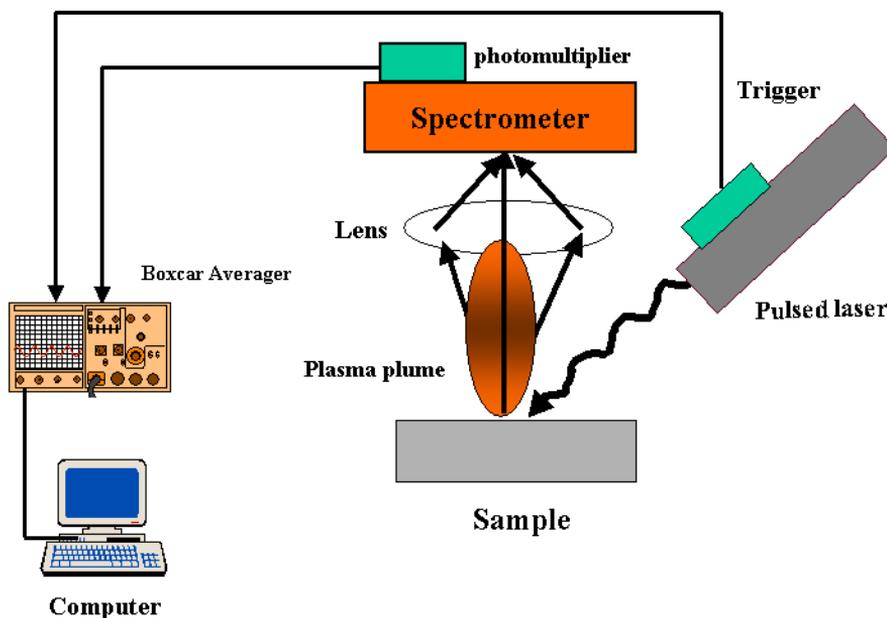
Due to the excellent features of LIBS, We have been motivated to develop a LIBS setup at our laboratory and the system has been successfully applied to analyze a variety

of rock and mineral samples. Atomic emission spectra of different trace elements present in the rock samples have been recorded in the 300–700 nm region.

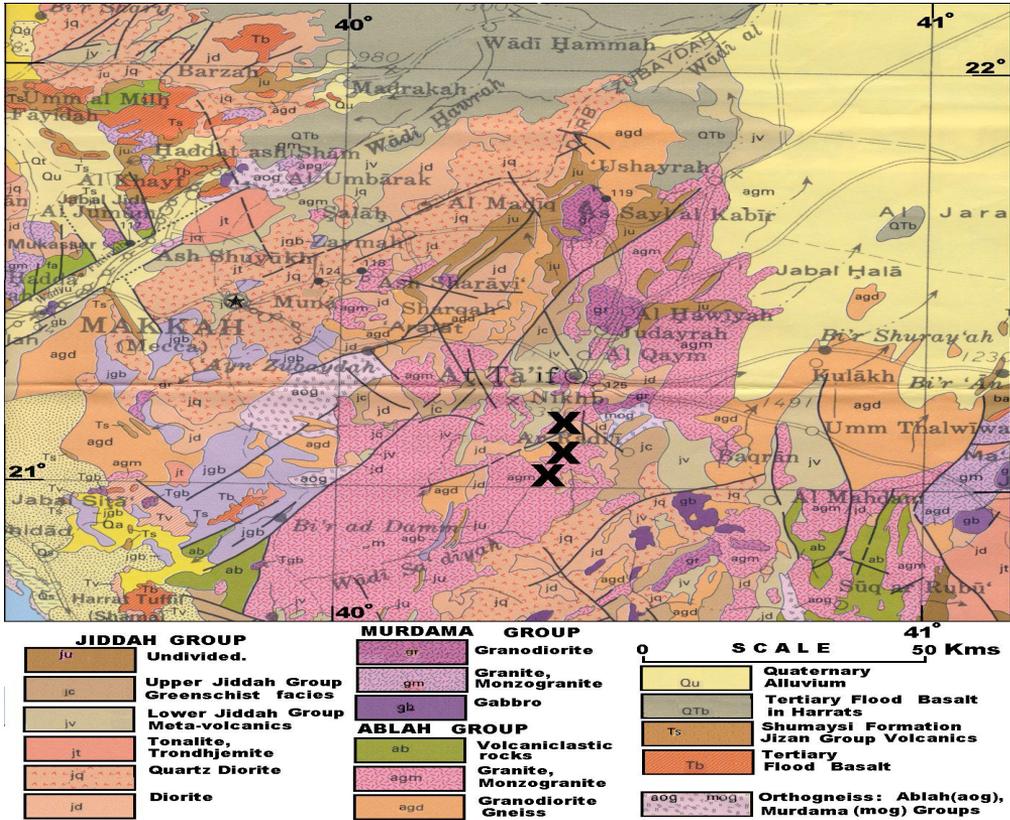
## 2. EXPERIMENTAL DETAILS

The experimental set up used for detection of laser induced breakdown spectra is presented in the Figure 1. A 308 nm (XeCl) laser radiation from a Lambda Physik Model EMG 203 excimer laser at an irradiance of  $7.6 \times 10^{10} \text{ W. cm}^{-2}$  was used. The laser pulse duration was typically of the order of 20 ns and repetition rate was 5 Hz. The average energy per pulse was  $\sim 80 \text{ mJ}$ .

The laser beam is focused on the surface of the sample to produce a laser spark (plasma). The sample was mounted on a rotary table to irradiate it at different spots. However, the samples can also be analyzed from pre-determined fixed spots without rotation of the sample. The atomic emission lines are recorded using grating monochromator (Spex 1875 with Compudrive CD 2A) and detected with thermoelectrically cooled photomultiplier (Thorne EMI 9558B). The electrical signal generated by photomultiplier was fed into Box-car averager (EG&G 4421) and processed by signal processor (EG&G 4402). The detection system averaged 5 pulses per sample point. The detection setup is described in detail in some earlier publications [Gondal et. al,1995a, Gondal et. al,1995b, Gondal et. al,1995c].



**Figure:1** Schematics of the experimental setup for the geological rock analysis



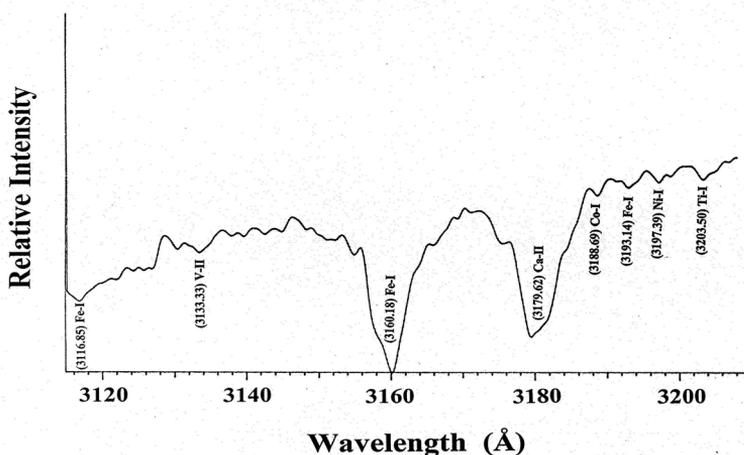
**Figure: 2** The location of the analyzed rock samples (marked by letter X), plotted on a part of the geological map of Saudi Arabia published by Brown et al. 1989.

### 3. RESULTS AND DISCUSSIONS

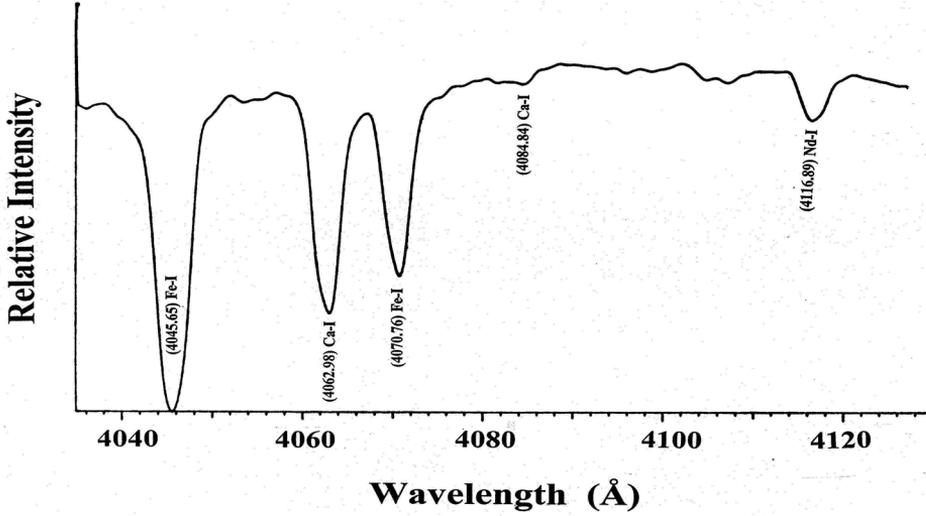
Identification of major and trace elements using LIBS has been conducted for the elements present in different rocks of geological interest collected from the southern part of At-Taif area. The location and geological setting of the rock samples analyzed in this study is shown Fig. 2. These samples are collected from the gabbroic to dioritic rocks, which are transected by mafic dikes as well as granitic pegmatites and intrusive breccias with granitic matrix. The outcrop is located about 10 kms south of At-Taif city, on the west side of Al-Shifa road. The meladiorites and mafic dike rocks contain accessory amounts of disseminated sulphide mineralization, dominated by pyrite and chalcocopyrite. These samples were studied petrographically to establish their mineral constituents, and to obtain a preliminary idea of the elements present. In the first step, the

monochromator was calibrated by recording the reference spectra of known elements such as mercury using the mercury lamp. Once the monochromator has been calibrated, then the laser induced breakdown spectra was recorded in the 300 -700 nm region. The identification of the spectrally resolved emissions was carried out by using the standard reference spectral lines of various elements and by calculating the corresponding transition wavelength using the energy levels available in the literature for such elements [Striganove et. al, 1968].

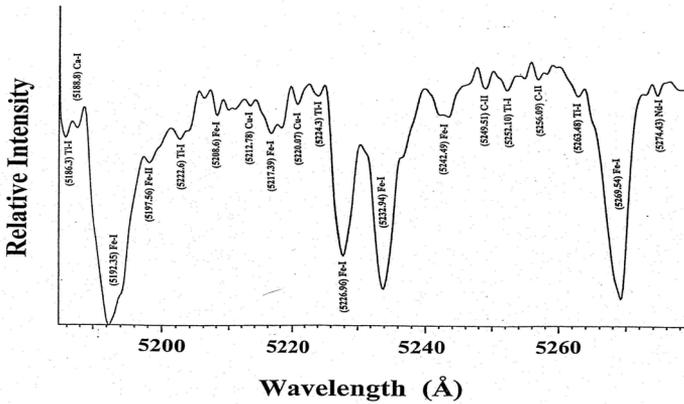
Typical spectra recorded with our setup in the UV and visible region is presented in figure 3-5. The observed spectral lines have been assigned to transitions in the neutral charge state of the corresponding atom of the material under investigation. The identification and the transition wavelength of recorded LIBS spectrum is presented in table 1. As shown in Table 1, many elements have been identified and it was found out that important elements such as Ni, Cu, Mg, Mo, Cr, K, Na, Ca and Fe have been detected from the samples from the Arabian shield rocks. These elements correspond to those expected on the basis of petrographic studies.



**Figure: 3** Typical spectrum recorded in the 3110- 3220 Å. Various elements present in the rock sample are indicated.



**Figure: 4** Typical spectrum recorded in the 4030- 4140 Å. Various elements present in the rock sample are indicated.



**Figure: 5** Typical spectrum recorded in the 5200 - 5280 Å. Various elements present in the rock sample are indicated.

**Table 1.** Identifiable elements in the wavelength range of 3116 – 8157 Å, employing LIBS.

Analytical Wavelength	Element	Analytical Wavelength	Element	Analytical Wavelength	Element
3116.85	Ru	4670.00	Mo	5227.24	Fe
3133.33	V	4673.53	Cu	5227.80	V
3160.18	Th	4677.61	Gd	5228.75	Sm
3179.62	Er	4682.43	Pr	5233.39	Er
3188.69	Dy	4688.93	Gd	5234.11	V
3193.14	Ce	4694.49	Kr	5234.19	Nd
3197.39	Os	4699.50	Cb	5241.89	U
3203.50	Cr	4704.50	Tb	5250.98	Ti/Mo,Fe
3259.26	Nd / In	4706.92	Sc	5251.07	Mo
3269.25	Fe/Mn	4712.29	Pr	5254.22	A
3277.39	Zr/Fe	4714.15	La	5257.00	Er
3284.61	Ta	4716.76	Si	5259.97	Ti
3290.53	Cu / V	4726.58	Nd	5260.80	Bi
3305.15	Zr/V	4734.55	yt	5264.15	Cr
3313.47	Tb / Mn	4788.93	Ne	5264.70	I
3524.81	Ti	4800.00	La	5264.79	Fe
3534.07	U	4802.78	Er	5265.18	I
3541.29	Dy	4816.02	Sm	5268.69	Ti/Co
3544.44	W	5106.31	Fe	5268.79	Gd
3552.77	I	5109.09	Sc	5268.96	Mo
3561.66	Hf	5123.37	Os	5277.12	Eu
3566.29	I	5126.34	Fe	5281.43	Ce
3569.25	Dy	5130.55	O	5281.75	Fe/Ni
3574.25	Ti	5137.65	Ru	5300.74	Kr
3581.47	Cs	5149.33	Eu	5314.90	Ce
3585.92	Mo	5154.90	W	5322.81	V
3595.54	Mo	5166.95	Th	5325.56	Fe
3610.17	Fe	5171.78	Os	5338.25	Eu
4045.65	Ne	5175.15	W	5346.71	Kr
4062.98	Ru	5183.71	Ti	5446.65	Ti
4070.76	V	5183.91	La	5455.47	Fe/Dy
4084.84	Tb	5184.57	Ni	5474.75	Nd
4116.89	Cb	5189.84	N	5487.23	V
4198.33	Fe	5192.42	Fe	5837.02	Nd
4201.13	U / Fe	5192.44	Fe	5843.50	Eu
4214.63	Nd / Mo	5193.29	Ne	5858.11	U/Fe
4227.22	Hg	5204.69	Fe	5888.20	Th , Mo
4236.3	Re	5208.95	Pd	5889.74	Na / Se
4238.89	Fe / Cr	5209.82	Nd	5891.02	Tb
4250.56	Fe / Kr	5211.00	Ce	5893.41	I
4261.48	Ce / Mo	5217.24	Fe,V	5895.07	Sb
4270.93	W	5217.26	Fe,	5896.39	Sm / Na
4288.89	U	5222.86	Hg	6278.52	Mo
4666.67	Ne	5226.95	Xe	6282.78	Ho

#### 4. CONCLUSIONS

The results achieved in this study show that it is feasible to apply the LIBS technique for the identification of trace elements in minerals and rocks. The technique could be also applied for trace pollutants in soil samples. The technique holds promise of wider utility because of its applicability under diverse conditions such as the remote analysis of in situ samples, microanalysis of small mineral grains, and simultaneous analysis of whole rocks and constituent minerals grains by the same method.

#### ACKNOWLEDGEMENTS

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