Analysis of acid pitchstone (Iceland) using laser induced breakdown spectroscopy (LIBS)

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Analysis of acid pitchstone (sample from Iceland) using laser induced breakdown spectroscopy (LIBS) is presented in this study. The rock sample was taken because of its uniform composition and a homogenous structure at microscale. Elements like Si, Fe, Ca, Mg, Al, Mn, Ti, Na, K, Ba, Sr and Li were detected in the LIBS spectra. Important plasma parameters (electron density and temperature) were calculated on the base of Stark broadening mechanism of spectral lines and Saha- Boltzmann plot method, respectively. Quantitative analysis was performed using calibration free (CF) approach of LIBS method. CF-LIBS analysis compared to reconstructed bulk rock analysis using precise mineral and glass analyses obtained by electron microprobe analysis (EMPA) gives a good correlation, sufficient enough for having primary information of chemical composition of the studied rock sample or alternatively large mineral phases. An element with very low atomic number, lithium, was detected only by LIBS. Li is not detectable on microprobe. Taking into account possible local mineral accumulations and imprecisions induced by estimation of mineral volumes in the glass the CF-LIBS method gives acceptably precise analyses for geological purposes.

Key words: Laser Induced Breakdown Spectroscopy, LIBS, plasma parameters, acid pitchstone

Introduction

A rock sample analysed using LIBS is a glass acid rhyodacite (pitchstone). The rock has a homogenous and a compact structure macroscopically. Fracture areas are of irregular shape with signs of conchoidal fracture but with matt appearance. Mineral shapes cannot be observed on fracture areas which indicate we are dealing with glassy dark, black rock with homogenous character in all its parts.

The glass rhyodacite sample was examined using electron microanalysator CAMECA SX100 with four wave-length dispersive spectrometers with high sensitive analysing crystals (State Geological Institute of Dionýz Štúr, Department of Special Laboratories, Bratislava, Slovak Republic). Glassy rhyodacite is mostly formed by matrix glass with microlithic clinopyroxene, plagioclase and magnetite. A glass and microlitic mineral analyses with the precision of 0.01 wt. % provide a reference analyses for LIBS accuracy evaluation as an analytical method.

Laser induced breakdown spectroscopy (LIBS) is a method of the optical emission spectroscopy, used for qualitative and quantitative analyses of samples in all physical states. High intensive and very short (~ ns) laser pulses focused on the sample surface are commonly used for the sample ablation. Although several types of lasers are used for LIBS, like N_2, CO_2, KrF or XeCl, the most frequently used are Q- switched pulsed Nd:YAG lasers. During the laser pulse duration is sample surface exposed to the energy density of hundreds of GW/cm^2. Small amount of the sample ablated from the surface is dissociated, atomized and partially ionized and plasma is being created. Formed plasma has short lifetime but reaches temperatures in the range of 0.5- 1.5 eV. Plasma cools down rapidly and spreads to the environment at supersonic velocities at the end of the laser pulse. Excited atoms and ions de-excite by light emission at characteristics wavelengths. Particular steps during the LIBS are depicted in Fig. 1. Using the spectrometer and detector, emission spectrum is recorded. Emission spectrum represents dependency between wavelength and relative intensity. Based on the lines position in the measured LIBS spectrum and available databases, it is possible to do the qualitative analysis of the sample under investigation. The concentration of given element presented in the sample is proportional to the integral intensity of spectral line, quantitative analysis can be done using only a measured LIBS emission spectrum.

A big advantage of LIBS method is rapidity, simplicity and also overall price of the parts of experimental apparatus. Laser induced breakdown spectroscopy is quasi- nondestructive analytical method (only small amount of sample, ~ tens of nanograms, is consumed during each laser pulse) which does not require special sample pre-treatment and therefore it is not necessary to handle with aggressive chemicals. Using the LIBS method it is possible to detect all elements of periodic table and also contemporary detection of various elements.

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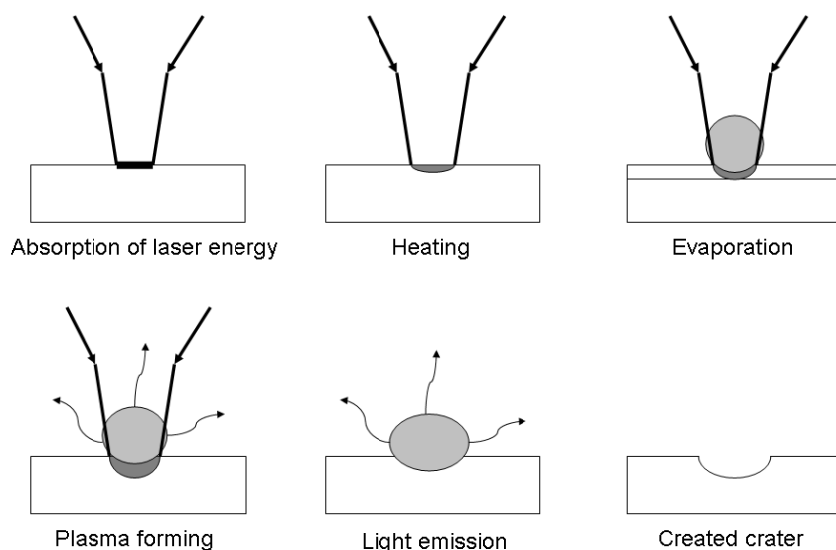
Fig. 1. Six steps of the LIBS process (Harmon R.S. et al., 2009).

Several aspects make LIBS a suitable method for qualitative and quantitative analyses in the field of geology, mineralogy or environmental application; i) possibility to miniaturize LIBS system, ii) components at an affordable price, iii) real-time analyses, iv) in-situ analyses, v) high sensitivity for low atomic mass elements which are hardly detectable using other spectroscopic techniques, vi) possibility of stand-off detection.

LIBS has been successfully used for analysis of geological materials, rock structure mapping, mineral analysis, remote analyses of different types of rocks and for qualitative as well as quantitative analyses of meteorites. Tucker J.M. et al., (2010) used it for remote (9 m), qualitative and quantitative analyses of 100 different igneous rocks. They tested a possibility of use of LIBS method for geochemical research of the surface of the planets in solar system. Novotný K. et al., (2008) used LIBS and LA-ICP-MS for granite surface mapping with the size of 20x20 mm^2 while observing four elements – Ca, Al, Fe, Mn. Harmon R.S. et al., (2009) deal with analysis of geomaterials and mineral differentiating using laser induced breakdown spectroscopy. In addition, portable LIBS devices are being used for analysis of geomaterials in the field research. Several of such devices are available on the market, e.g. Easy LIBS by IVEA©, PL100-GEO by Applied Spectra©, LIBSCAN 25 by Applied Photonics©, Porta-LIBS-2000 by StellarNet Inc.©, IDEALIBS by Bertin Technologies©. However, many of them weigh up to 25 kg. Rakovský J. et al., (2012) present portable LIBS device (Fig. 2) weighing only 5 kg in their work. System and computer battery life limits working time of the device which reaches approximately 6 hours. The device was tested on geological samples (ammonites and lacustrine sediments) and was also used for analysis of volcanic ash (Rakovský J. et al., 2011). More information about this device can be found at: http://www.ivea-solution.com/libs/product_info.php?cPath=25&products_id=50. Portable LIBS device was used for detection of lead content in the sediment samples taken from a road in the tunnel „Cerrado de Calderon" by Cunat J. et al., (2009). LIBS method was used for fast and precise identification of silicate and carbonate minerals by McMillan N. et al., (2007). Dell' Aglio M. et al., (2010) and De Giacomo A. et al., (2007) present LIBS results of analyses of different types of meteorites (Dhofar 019, Dhofar 461, Sahara 98222, Toluca, Sikhote Alin, Chondrit L6, Campo del Cielo). They pointed out that LIBS can be successfully used for identification and classification of meteorites.

Within the participation in the project of plasma drilling machine development, our aim is to obtain as much knowledge as possible about plasma (temperature and electron density) formed above the

Fig. 2. Portable LIBS device used by Rakovský J. in his dissertation thesis.

surface of selected examined model material (acid rhyodacite glass) as well as its interaction with the material surface. Although plasma was generated in laboratory conditions, it is sufficient for testing of rock resistance to formed plasma as well as for model creation. Qualitative and quantitative analysis was performed on the glass rhyodacite sample and dependence of size and depth of the crater on the laser pulse energy was examined.

Experimental part

The block diagram of experimental LIBS setup is shown in Fig. 3. Pulsed Nd^{3+}:YAG laser (Brilliant EaZy, Quantel), running at second harmonic frequency with pulse duration of 4 ns and maximal energy of 165 mJ/pulse was used as a laser ablation source. Laser beam was directed and focused on the sample surface using optical prism and lens with the focal length of 40 mm. The emission of formed plasma was focused into 1 meter long optical fibre using another lens and the fibre was attached to the input slit of emission echelle spectrometer (Mechelle ME 5000, Andor Technology). This type of spectrometer is able to cover wide spectral range from 200 nm to 975 nm and has a spectral resolution $\lambda/\Delta\lambda = 5000$. Intensified CCD camera (iStar DH 734, Andor Technology) was used for emission spectra detecting. Examined samples were placed at the translation stage which allows adjusting the sample in all directions. Calibration mercury-argon lamp was used for calibration of spectrometer wavelengths. All measured spectra were corrected according to the spectral response curve of the echelle spectrometer.
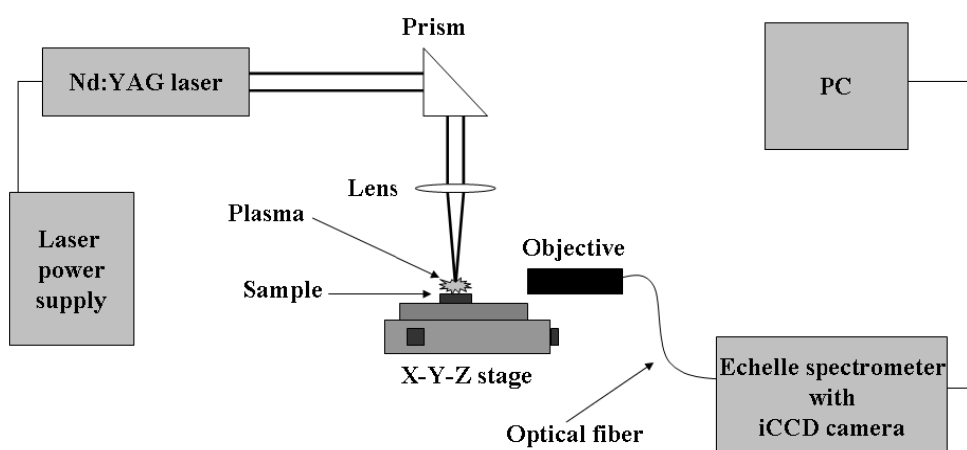

Fig. 3. The block diagram of experimental LIBS setup.

Qualitative analysis

Qualitative composition of glass rhyodacite was determined on the basis of emission LIBS spectra and available databases. Silicon, iron, magnesium, sodium, potassium, aluminium, calcium, titanium, manganese, barium and lithium were detected using LIBS (Fig. 4). Detected oxygen could come from the examined sample but also from the ambient air because of the measurements were carried out in the air at atmospheric pressure. Nitrogen and hydrogen were also identified, however, they come from the ambient air.

All of the above-mentioned elements expect Li (which cannot be analysed using EMPA) were analysed using electron microprobe analysis (EMPA) and the analysis was extended by elements Cl, Cr, F, Sr and V.

Electron concentration determination

Coming from the assumption that Stark broadening is a dominant mechanism of spectral lines broadening in our conditions, according to Gigosos M.A. et al., (2003) we can determine the electron density using the expression

$$FWHA = 0.549nm \times \left(\frac{N_e}{10^{23}m^{-3}}\right)^{0.67965} \tag{1}$$

where parameter FWHA means full width at half area of a peak and Ne is electron density. Hydrogen spectral line Hα (656 nm) was used for calculation of the electron density. We obtained FWHA parameter

by fitting this spectral line by Lorentzian profile and subsequently determined the electron density Ne. The average value of electron density determined by expression (1) is (1.3E23 ± 0.15) m^{-3}.
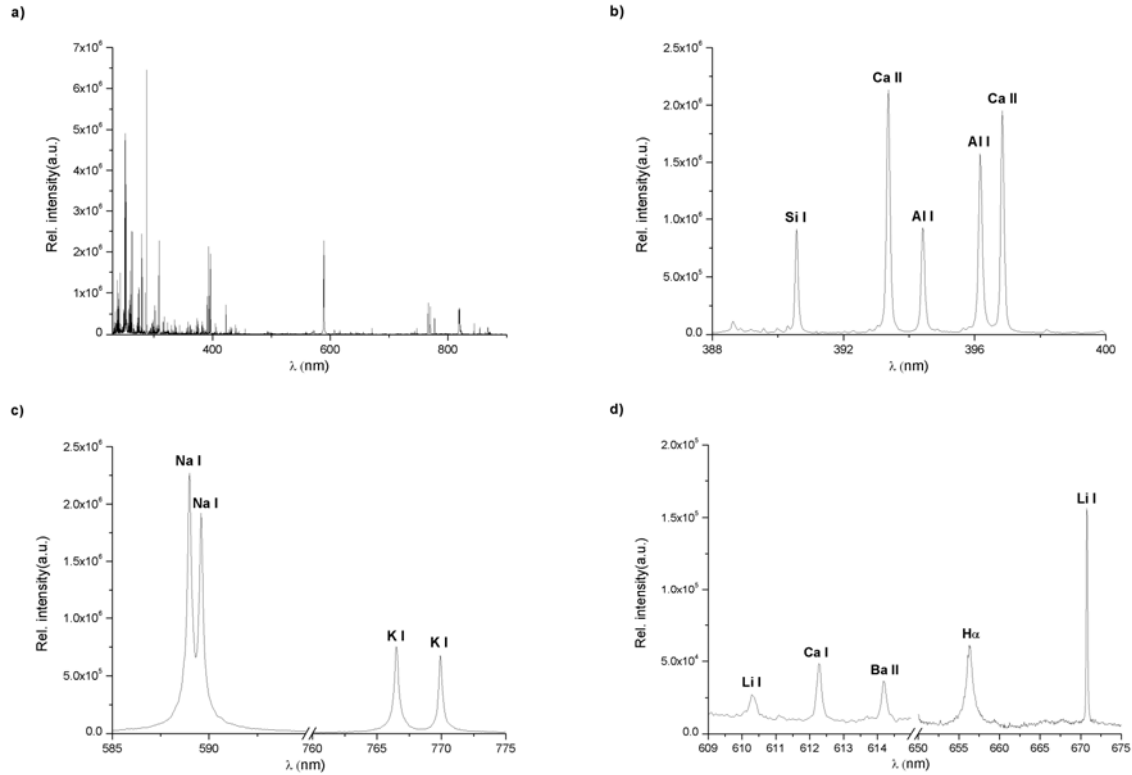

Fig. 4 a) Overall LIBS spectrum of pitchstone in the wavelength range of 230-900 nm recorded as an accumulation of 50 laser shots, b) neutral spectral lines of silicon, aluminium and singly ionized lines of calcium, c) neutral spectral lines of alkali metals (Na and K), d) neutral spectral lines of lithium and calcium, singly ionized line of barium and hydrogen alpha line used for electron density calculation.

Electron temperature determination

We can determine electron temperature using Saha-Boltzmann diagrams assuming that plasma is optically thin and is in a state of local thermodynamic equilibrium (LTE) which is often expressed by the so-called McWhirter criterion

$$N_e \geq 1.6 \times 10^{12} T^{1/2} (\Delta E)^3 \, cm^{-3} \tag{2}$$

where T (K) is electron temperature and ΔE (eV) is the biggest difference between two energy levels while the LTE condition is still valid. X- and y- axis coordinates of the Saha-Boltzmann diagrams are calculated by following expressions (Tognoni E. et al., 2007)

$$x = \begin{cases} E_k \\ E_j + E_{ion} \end{cases} \tag{3a,b}$$

$$y = \begin{cases} \ln\left(\dfrac{I_{ki}\lambda}{A_{ki}g_k}\right) \\ \ln\left(\dfrac{I_{jh}\lambda}{A_{jh}g_j}\right) - \ln\left(\dfrac{2(2\pi m_e)^{3/2}(k_B T_e)^{3/2}}{n_e h^3}\right) \end{cases} \tag{3c,d}$$

where E_k denotes energy of the corresponding energy level, E_{ion} is ionization energy , I denotes integral intensity of spectral line, λ is wavelength, A is Einstein coefficient of transition probability, g is statistical weight, m_e is electron mass, k_B Boltzmann constant, T_e electron temperature, n_e is electron density and h is Planck constant. The advantage of Saha-Boltzmann diagrams is that it enables to plot the coordinates for neutral (3a, c) as well as singly ionized (3b, d) atoms. This increases the accuracy of the electron temperature

determination. We can determine the electron temperature T_e from the slope of linear fit line through the points in Saha-Boltzmann diagram which is proportional to $-1/k_B.T_e$. Saha-Boltzmann diagram for three different elements is shown in Fig. 5. Electron temperature values determined for various elements are summarized in Tab.1.
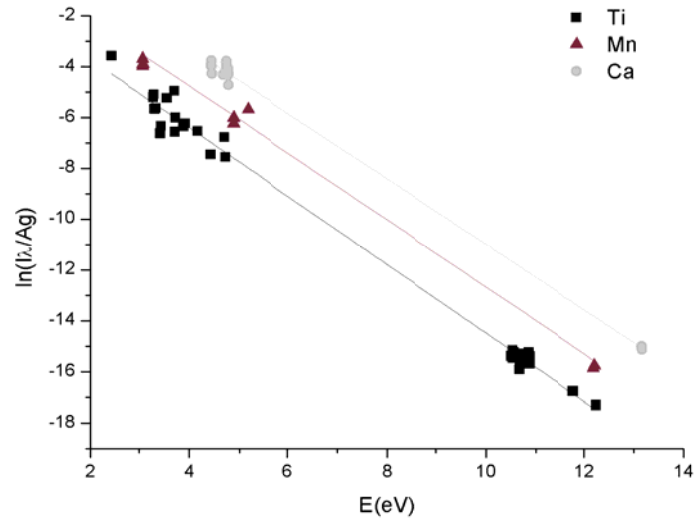

Fig. 5. Saha-Boltzmann diagram for titanium, manganese and calcium used for the electron temperature calculation.
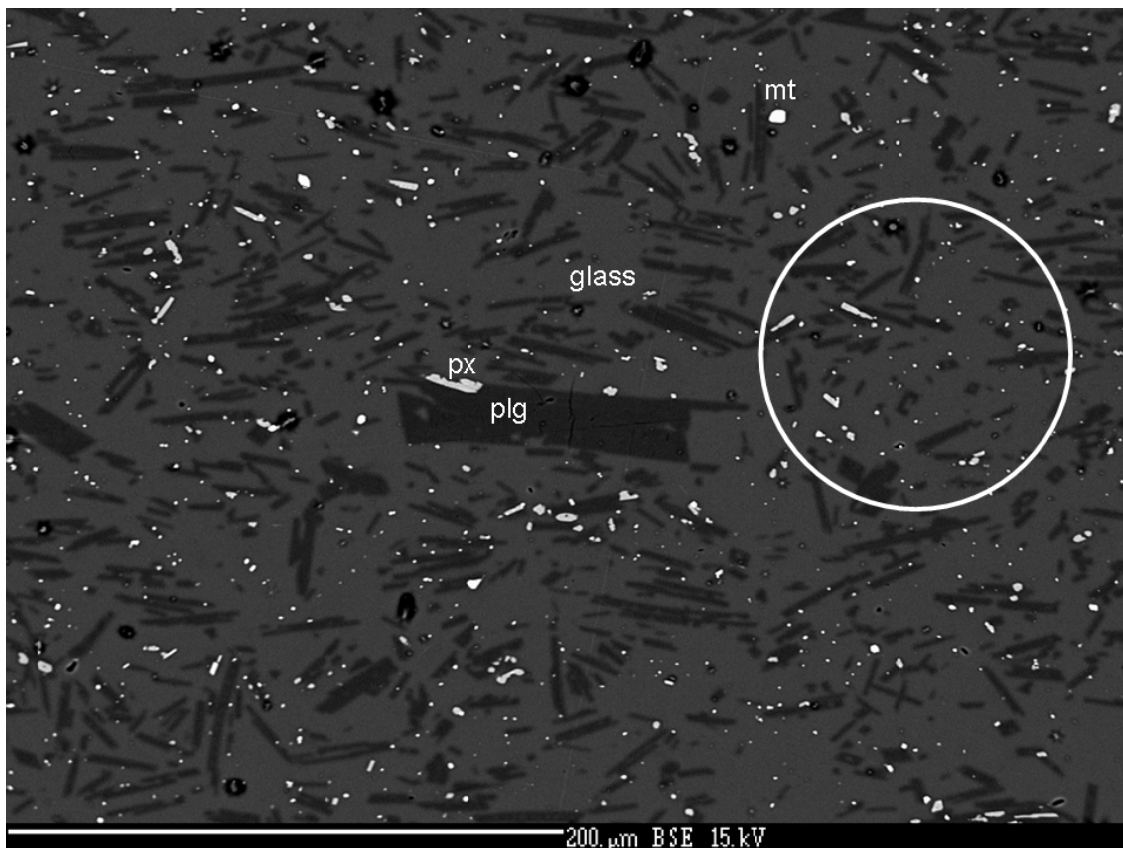

Fig. 6. Analysed minerals in the pitchstone (px- pyroxene, plg- plagioclase, mt- magnetite, glass- matrix), image of back-scattered electrons (BSE), white circle approximates area ablated by LIBS measurements.

Quantitative analysis

When LTE condition described by the expression (2) is fulfilled and the plasma is optically thin, intensity of spectral line can be described by the following expression

$$I_\lambda^{ki} = A_{ki} n_k^s = A_{ki} n^s \frac{g_k e^{\frac{-E_k}{k_B T_e}}}{U^s(T)} \tag{4}$$

where n_k^s is the population density of excited energy level k with s particles, n^s is the total concentration of s particles and $U^s(T)$ is a partition function at temperature T, other symbols have been described in previous sections. As you can see from the expression (4), particle concentration is proportional to spectral line intensity so we can carry out qualitative as well as quantitative analysis from the measured LIBS spectrum.

The method used for element concentration determination in examined samples is called calibration free laser induced breakdown spectroscopy (CF-LIBS). As the name of the method might say, no reference standards are needed for concentration determination so we do not experience the problems such as the matrix effect. On the other hand, precise plasma parameters determination is required in order to accurately determine the concentrations of particular elements. The CF-LIBS method is well-described in Tognoni E. et al., (2007).

Tab. 1. The electron temperature determined using Saha-Boltzmann plot method of various elements.

Element	Te [eV]
Iron	0.81
Manganese	0.76
Titanium	0.74
Calcium	0.75
Magnesium	0.78
Average	0.77

*Tab. 2. Analyses of pitchstone mineral phases and matrix glass using EMPA, concentrations are given in weight %. **N** is the number of analyses for average. Area (%) is planimetric analysis of BSE image of the pitchstone, where mineral abundances are given in percent. These abundances and mineral composition were used for estimation of bulk rock analysis (see Table 3). Routine precision of EMPA analyses is 0.01 wt. %.*

N	6	5	6	4	1
	glass	plagioclase	clinopyroxene	olivine	titanomagnetite
Na₂O	3.75	7.93	0.34	0.04	
SiO₂	73.58	66.24	49.28	31.46	0.62
Al₂O₃	11.92	20.21	1.23	0.09	1.22
MgO	0.14	0.01	6.4	6.94	0.44
Cl	0.17	0.03	0	0	
K₂O	4.24	1.92	0.11	0.06	
CaO	0.9	2.6	12.57	0.5	0.06
TiO₂	0.31	0.09	0.39	0.07	13.21
FeO	4.11	0.8	27.51	56.47	75.51
MnO	0.16	0.03	1.93	3.2	1.14
Cr₂O₃	0.01	0	0.01	0	0
NiO	0.01	0.05	0	0	0
BaO		0.19			
ZnO					0.26
V₂O₃					0.03
Total	99.31	100.11	99.78	98.84	92.48
Area[%]	78.4	20.0	1.0	0.5	0.1

The resulting analysis using average of five CF-LIBS spots is presented in Tab. 3. LIBS analysis cannot be considered as point analysis because the size of the spot (ablated sample by laser beam) is approximately 100x100 μm in dependence of used beam energy. Average CF-LIBS analysis represents bulk-rock pitchstone analysis.

Pitchstone was for a reference analysed by electron microprobe. The back scattered electron images (BEI) revealed, that the pitchstone is composed by prevailing glass, needle-like or long tabular plagioclase, small euhedral or prismatic clinopyroxene and olivine and tiny euhedral titanomagnetite (Fig. 6). All mineral phases are microlithic, plagioclase is the largest one with dimensions about 10-30 μm, the other minerals are 1 to 10 μm in average. Electron microprobe is capable to analyse with an electron beam focused

to up to 0.5 μm, though all mineral phases and matrix glass were analyses at few places with a beam diameter 1 to 5 μm. Beam diameter extended to 10 μm was used for analyses of the glass. Concentrations of elements of mineral phases in weight % of oxides acquired by EMPA method are summarized in Tab. 2. BEI images provide information on space distribution of all mineral phases. An image analysis program calculated the areas (planimetric analysis) belonging to mineral phases. Using mineral abundances and chemical composition of the mineral phases we were able to calculate bulk-rock analysis (Tab. 2 and 3).

*Tab. 3. Average bulk-rock CF-LIBS analysis using five spots compared to calculated bulk-rock EPMA analysis using precise analyses of mineral phases and abundances (listed in Table 2) derived from BSE image by image analysis software. Symbol * denote estimated Li2O concentration due to the low number of spectral lines presented in the measured LIBS spectra. CF-LIBS analysis was normalised to 100 wt. % (method gives a relative concentrations of elements).*

	CF-LIBS measurements	EMPA bulk-rock
Na_2O	5.45	4.53
SiO_2	68.04	71.6
Al_2O_3	16.61	13.41
MgO	0.27	0.20
Cl		0.14
K_2O	3.41	3.71
CaO	1.80	1.35
TiO_2	0.45	0.28
FeO	3.65	4.00
MnO	0.08	0.17
Cr_2O_3		0.01
NiO		0.02
BaO	0.03	<0.01
ZnO		<0.01
V_2O_3		<0.01
Li_2O	0.20*	
Total	99.99	99.42

Conclusion

Laser induced breakdown spectroscopy (LIBS) method was used for glass rhyodacite (pitchstone) analysis. The composition of pitchstone samples was determined based on measured emission spectra, and precise determination of plasma parameters; electron density in the formed plasma using Stark broadening mechanism and electron temperature using Saha-Boltzmann plot method. Quantitative analysis of examined samples was performed using calibration-free laser induced breakdown spectroscopy (CF-LIBS). Elements such as Si, Fe, Al, Ti, Ca, Mg, Ca, K, Na and Ba were quantified in examined samples of rhyodacite. Quantitative analysis of examined material was also performed using more precise conventional method; electron microprobe analysis (EMPA). The results obtained by CF-LIBS were compared to the results obtained by EMPA and we can conclude that the average CF-LIBS results correspond to the results of EMPA.

Based on the achieved results we can state that LIBS method is suitable for determination of plasma parameters and for qualitative and quantitative analysis of geologic materials. The possibility of miniaturizing of the system predetermines this method to be suitable for fast, simple, qualitative and quantitative analysis of not only the geologic samples in the field research.

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