Sikhote-Alin Meteorite, Elemental Composition Analysis Using CF LIBS

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Abstract. Calibration free laser induced breakdown spectroscopy (CF-LIBS) method was used for determination of elements presented in meteorite Sikhote Alin as well as its quantities. As a source of ablation, Q-switched Nd: YAG laser operating at 532 nm was used. Emission from plasma was collected by optical fiber that was connected with slit of Echelle spectrometer (ME 5000, Andor) coupled with iCCD camera (iSTAR DH734i-18F-03, Andor). Optimal experimental conditions, i.e. time delay, gate width, energy per pulse were found. The measured spectra were recorded 2.5 μs after laser pulse and gate width of iCCD camera was set to 0.5 μs. Electron concentration was calculated from broadening of hydrogen Hα line (656 nm). A Saha-Boltzmann plot method was used for determination of electron temperature, assuming the local thermodynamic equilibrium. Apart from iron, which is the main elemental constituent of examined meteorite, elements like nickel, cobalt, phosphor, potassium, sodium, calcium and manganese, were also detected. In comparison with official Sikhote Alin elemental quantitative measurements, some elements like sodium, calcium, potassium and manganese were not mentioned, it is expected that these elements were added to the surface of meteorite after the meteorite fall.

Introduction

Laser induced breakdown spectroscopy (LIBS) is an analytical technique of optical emission spectroscopy (OES) used for qualitative and quantitative analysis of materials in the solid, liquid and gaseous phase and aerosols. In LIBS, plasma is formed using high intensive laser pulse focused on the sample surface and emission from plasma spark is collected by optical fiber linked with emission spectrometer. Plasma emission contains information of elemental sample composition, because every element has unique spectrum with characteristic wavelengths.

CF-LIBS is quantitative LIBS approach use for analysis of solid samples is described in details in (*Tognoni et al., (2007)*). Calibration free means no reference standard materials are required and no calibration curves are constructed for elemental quantification. On the other hand, precise determination of electron density and temperature are needed for precise determination of elemental concentration. Determination of these two parameters is crucial point in the CF-LIBS analysis. Several methods are known for determination of plasma electron density and temperature. When electron impact parameters are known, electron density can be calculated using Stark broadening mechanism (*Aragón et al., (2010)*). Also broadening of hydrogen Balmer series lines are used for electron density calculation (*Gigosos et al., (2003)*). For determination of electron temperature Boltzmann or Saha-Boltzmann plot methods are usually used (*Aguilera et al., (2007)*).

LIBS and CF-LIBS were successfully applied for analysis of different types of solid materials, i.e. geological samples (*Kaski et al., (2003)*), soils (*Corsi et al., (2006)*), sediments (*Lazic et al., (2001)*) and also meteorites (*Colao et al., (2004)*).

Analyses of multielemental samples are usually time-consuming and carried out by complex analytical methods such as atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), etc. These methods require the use of reference standard samples and digestion procedure, therefore the analysis of big amount of multielemental samples may take long time and can be expensive. Hence CF-LIBS method is applied for meteorite analysis, because it is fast, non-destructive and does not require sample pretreatment. Moreover, in LIBS and CF-LIBS analyses, any manipulation or treatment with chemicals is needed; therefore possibility of sample contamination is minimized.

In this work, possibility of CF-LIBS as a spectroscopic technique suitable for qualitative and quantitative analysis of meteorite Sikhote Alin is discussed.

Experimental setup

Scheme of experimental apparatus used for meteorite Sikhote Alin measurements at atmospheric pressure is shown on Figure 1. Q-switched Nd:YAG laser (Brilliant EaZy, Quantel) operating at 532 nm wavelength was used for plasma generation, with 5 ns pulse duration and maximum energy per pulse of 165 mJ. Laser beam was focused on the sample surface by convex lens (N-BK 7, with antireflex coating for 532 nm, focal length of 50 mm) to a point with diameter of 0.1 mm. Sample was placed on holder which was able to move in x, y, z directions. During each laser pulse about tens of ng of material was ablated from the sample surface and crater with 500 μm diameter was created. Plasma emission was focused by convex lens (CaF$_2$, focal length of 40 mm) into the optical fiber connected with entrance slit of Echelle type spectrometer (Mechelle ME 5000, Andor) coupled with iCCD camera (iStar, Andor). Intensified CCD camera was cooled down to –15°C to eliminate thermal noise from the camera chip. Wavelength calibration was done with mercury- argon calibration lamp (HG 1, Ocean Optics) and spectral sensitivity was measured using wolfram lamp—for wavelengths range from 400 nm to 900 nm, with NO^{2+}, OH and 2PS systems and deuterium lamp for wavelengths range from 200 nm to 400 nm. Measurements were carried out in air at atmospheric pressure. PC was used for data acquisition and analysis. Before analyzing process all measured spectra were corrected using the spectral response curve of echelle type spectrometer.

Measurements

One of very numerous fragments of mentioned meteorite was analyzed in our laboratory. Its volume was approximately 1cm^3. In order to eliminate possible inhomogenities in meteorites structure, LIBS spectra taken from different parts of meteorite, after each set of laser shots, the spot was changed. Spectrometer was set to start collecting emission 2.5 μs after laser pulse and the gate width was set to 0.5 μs. First the system, meaning laser beam focus, meteorite and focus of emission collecting lens was fine tuned to receive best possible signal to noise ratio. Then spectrum for each spot on meteorite was taken. Spectrum for each spot consists of 100 laser shots.

Measured spectra were analyzed using program that was developed in our laboratory. All measured spectra were loaded into program and then all peaks were recognized. To each peak an element and its degree of ionization was assigned and finally theoretical data such as Einstein coefficient A_{ik}, degeneration of level g_i, g_k, lower and upper energy levels E_i, E_k, theoretical wavelength, from NIST atomic lines database (*Ralchenko et al.,(2012)*) and Harvard database (*Kurucz et al., (1995)*) was loaded to list of spectral lines.

Theory

Determination of electron concentration

Main broadening mechanism presented in laser induced plasmas is Stark broadening mechanism caused due to collisions between charged particles. Broadening of spectral lines is used for
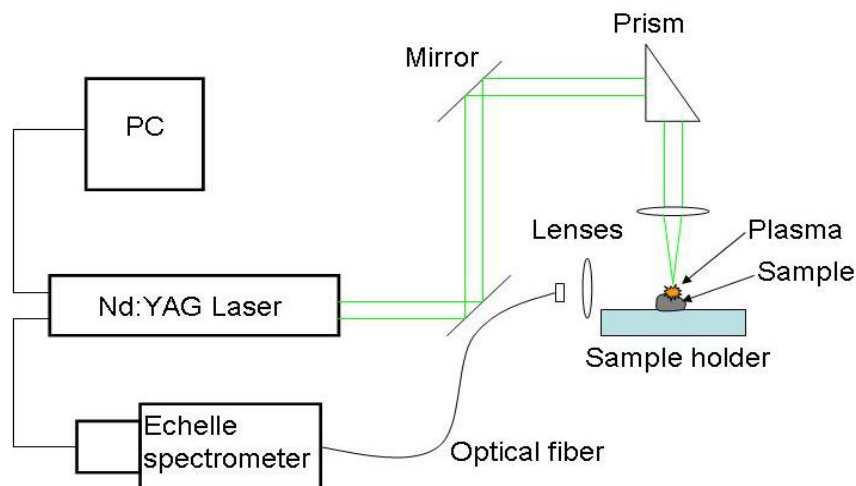
Figure 1. Experimental setup.

determination of electron density. Generally, full width at half maximum parameter (FWHM) is used, but this parameter is much more sensitive to ion dynamics effects (*Gigosos et al., (2003)*). Therefore full width at half area (FWHA) parameter was used for determination of electron density from hydrogen Balmer Hα line (656 nm) using equation

$$FWHA = 0.549 \times 10^{-9} \times \left(\frac{N_e}{10^{23}}\right)^{0.67965}$$

where N_e is unknown electron density in m^{-3}, FWHA is measured in *nm*.

Determination of electron temperature

For determination of electron temperature several techniques are used, i.e. line to continuum intensity ratio, Boltzmann plots, Saha-Boltzmann plots. When local thermodynamic equilibrium expressed condition expressed by McWhirter criterion

$$N_e \left(\text{cm}^{-3}\right) > 1.6 \times 10^{12} T^{1/2} \left(\Delta E_{nm}\right)^3$$

is fulfilled, Saha-Boltzmann plot method can be applied for electron temperature calculation. This method of determination of electron temperature from optical emission is described in details in (*Aragón C. et al. (2008).* Knowing intensities and table values for each spectral lines used for calculation one could create for each measured spectra SB diagrams using these formulas

$$x = \begin{cases} E_k & \text{for neutral lines} \\ E_j + E_{ion} & \text{for ionic lines} \end{cases}$$

$$y = \begin{cases} \ln\left(\dfrac{I_{ki}\lambda}{A_{ki}g_k}\right) & \text{for neutral lines} \\ \ln\left(\dfrac{I_{jh}\lambda}{A_{jh}g_j}\right) - \ln\left(\dfrac{2(2\pi m_e)^{3/2}(k_B T)^{3/2}}{h^3 N_e}\right) & \text{for ionic lines} \end{cases}$$

where E_k, E_j are energies of upper energy state, E_{ion} is ionization energy, I_{ki} is intensity of emission line of transition from energy level k to energy level i, g_k is the factor of degeneration of energy level, m_e electron mass, k_b Boltzman constant, T is temperature of electrons (estimated), h Planck constant N_e is concentration of electrons.

Electron temperature can be then determined from the slope of linear fit in the S-B plot. Slope of the linear fit is equal to $-1/k_B.T_e$.

Results

Qualitative analysis

Emission lines in measured spectra were used for qualitative analysis of meteorite Sikhote AlinSpectral lines of different elements were identified in the measured spectra by means of program, in which two atomic lines databases: NIST (*Ralchenko et al., (2012)*) and Kurucz-Harvard (*Kurucz et al.,(1995)*) were implemented. Typical spectral lines, so called "finger prints" of given element, of iron (Figure 2a)), nickel (Figure 2b)), calcium (Figure 2c)), potassium (Figure 2d)), manganese (Figure 2e)), sodium (Figure 2f)) were found in measured spectra and then we can clearly achieve their presence in meteorite fragment. Also spectral lines presented in air like oxygen (spectral lines at 777 nm and 844 nm), nitrogen (strong lines at 742 nm, 744 nm and 746nm) and hydrogen (Hα line at 656 nm) were observed in measured spectra because measurements were carried out in air at atmospheric pressure. Therefore if these elements are presented in meteorite fragments we are not able to quantify them. Calculated relative quantities of elements in ablated plasma are summarized in Tab. 1.

Conclusion

In this work possibility of use of calibration free laser induced breakdown spectroscopy for

meteorite quantitative analysis is presented. Several fragments of meteorite Sikhote Alin were analyzed by means of CF-LIBS. Concentrations of major (Fe) and minor (Ni, Co, P, Na, K, Ca, Mn) elements were calculated. For more accurate determination of element concentration, correction of selfabsorption effect was done by taking into account several parameters, i.e. Einstein coefficients for stimulated emission and absorption, energy of upper level, population density of lower level, relative ratio between neutral and singly ionized particles in laser induced plasma and preliminary determined concentration of element. Taking into account these parameters, several spectral lines were rejected from analysis and Saha-Boltzmann plots were constructed without use of these spectral lines.

Because analysis were carried out in air at atmospheric pressure, concentration of elements which are presented in air and also in meteorite fragments i.e. oxygen, nitrogen and hydrogen and were not achieve in concentration calculation. Therefore complete analysis could be done using another atmosphere in the vacuum chamber, e.g. helium or argon.

**Table 1.** Relative concentration of elements presented in ablated plasma.

	spot 1	spot 2	spot 3	spot 4	spot 5	Average
Fe	89.2%	88.1%	87.9%	87.5%	87.4%	**88.0%**
Ni	5.3%	5.5%	6.2%	5.4%	4.2%	**5.3%**
Co	1.2%	2.9%	2.2%	3.5%	1.9%	**2.3%**
P	1.1%	0.3%	0.7%	1.5%	0.5%	**0.8%**
Na	1.4%	0.9%	0.9%	1.2%	1.9%	**1.3%**
K	0.5%	1.0%	0.6%	0.3%	1.2%	**0.7%**
Ca	1.3%	1.0%	1.4%	0.6%	2.6%	**1.4%**
Mn	0.0%	0.2%	0.1%	0.1%	0.4%	**0.2%**
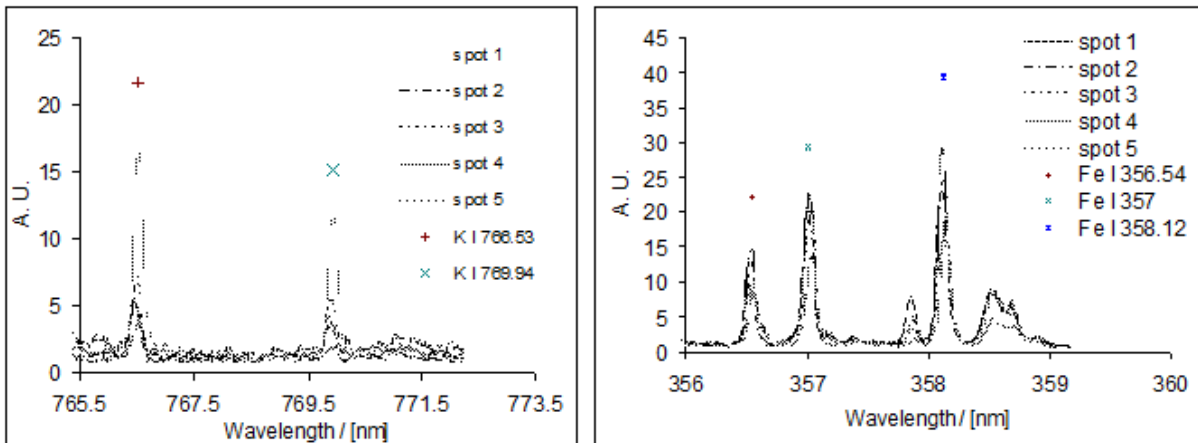
Figure 2. Typical spectral lines so-called "finger prints" of elements for Fe, K.
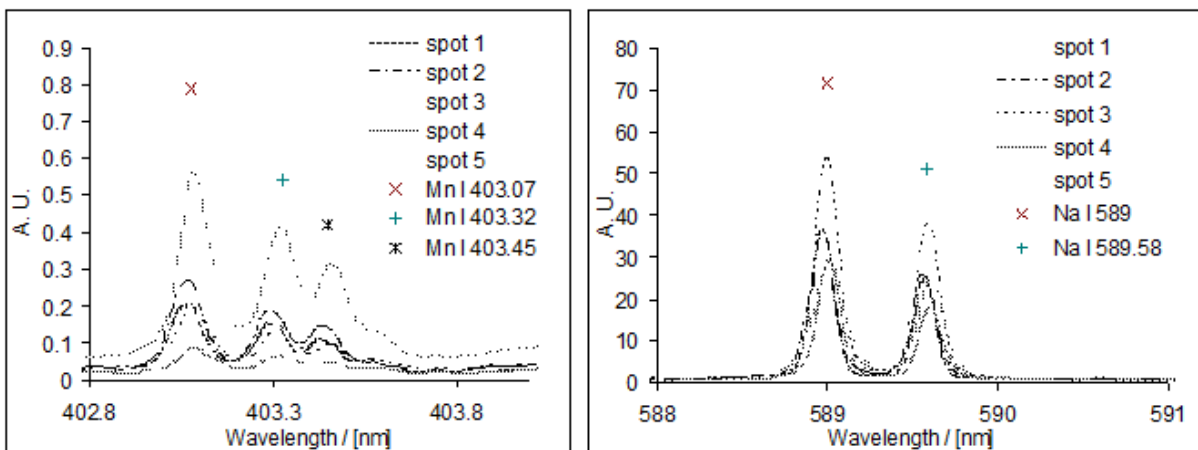
Figure 3. Typical spectral lines so-called "finger prints" of elements for Mn , Na.
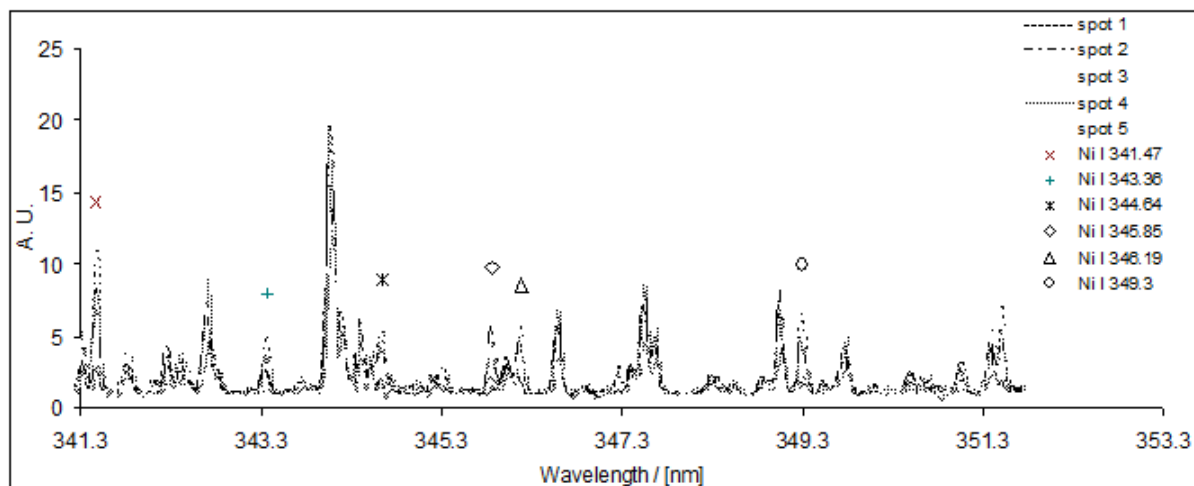
Figure 4. Typical spectral lines so- called "finger prints" of elements for Ni.

We can conclude, CF-LIBS is suitable method for analysis of meteorite samples because comparing with other analytical method, it is fast, non destructive, does not require sample preparation and only small amount of the sample is consumed during the measurements. Presented results (Tab. 1), achieved only by one method LIBS, correspond with these obtained by various experimental groups over the world.

References

J. A. Aguilera, C. Aragón, Multi-element Saha–Boltzmann and Boltzmann plots in laser-induced plasmas, Spectrochimica Acta Part B 62 (2007) 378–385.

C. Aragón , J. A. Aguilera, Characterization of laser induced plasmas by optical emission spectroscopy: A review of experiments and methods, Spectrochimica Acta Part B 63 (2008) 893–916.

C. Aragón, J. A. Aguilera, Determination of the local electron number density in laser-induced plasmas by Stark-broadened profiles of spectral lines Comparative results from Hα, Fe I and Si II lines, Spectrochimica Acta Part B 65 (2010) 395–400.

M. Corsi, G. Cristoforetti, M. Hidalgo, S. Legnaioli, V. Palleschi, A. Salvetti, E. Tognoni, Ch. Vallebona, Double pulse, calibration-free laser-induced breakdown spectroscopy: A new technique for in situ standard-less analysis of polluted soils, Applied Geochemistry 21 (2006) 748–755.

F. Colao, R. Fantoni, V. Lazic, A. Paolini, F. Fabbri, G. G. Ori, L. Marinangeli, A. Baliva, Investigation of LIBS feasibility for in situ planetary exploration: An analysis on Martian rock analogues, Planetary and Space Science 52 (2004) 117–123.

M. A. Gigosos, M. A. González, V. Cardenoso, Computer simulated Balmer-alpha, -beta and -gamma Stark line profiles for non-equilibrium plasmas diagnostics, Spectrochimica Acta Part B 58 (2003) 1489–1504.

S. Kaski, H. Häkkänen, J. Korppi-Tommola, Sulfide mineral identification using laser-induced plasma spectroscopy, Minerals Engineering 16 (2003) 1239–1243.

R. L. Kurucz and B. Bell, (1995) Atomic Line Data, Kurucz CD-ROM No. 23. Cambridge, Mass.: Smithsonian Astrophysical Observatory.

V. Lazic, R. Barbini, F. Colao_, R. Fantoni, A. Palucci, Self-absorption model in quantitative laser induced breakdown spectroscopy measurements on soils and sediments, Spectrochimica Acta Part B 56 (2001) 807–820.

Yu. Ralchenko, Kramida, A.E., Reader, J., and NIST ASD Team (2011). NIST Atomic Spectra Database (ver. 4.1.0), [Online]. Available: http://physics.nist.gov/asd [2012, National Institute of Standards and Technology, Gaithersburg, MD.

E. Tognoni, G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti, M. Mueller, U. Panne, I. Gornushkin, A numerical study of expected accuracy and precision in Calibration-Free Laser-Induced Breakdown Spectroscopy in the assumption of ideal analytical plasma, Spectrochimica Acta Part B 62 (2007) 1287–1302.