

Elemental fractionation and quantification of geological standard samples by nanosecond-laser ablation

Tao Lü^{a,b,*}, Yang Hu^{a,1}, Zihan Li^a, Jiuling Meng^b, Changjiang Zhang^a, Zhaochu Hu^b, Yongsheng Liu^b

^a School of Mathematics and Physics, China University of Geosciences, Wuhan 430074, China

^b State Key Laboratory of Geological Process and Mineral Resources, Faculty of Earth Sciences, China University of Geosciences, Wuhan 430074, China

ARTICLE INFO

Article history:

Received 30 October 2017

Received in revised form 23 February 2018

Accepted 28 February 2018

Available online xxx

Keywords:

Laser-induced breakdown spectroscopy (LIBS)

Elemental fractionation

Geological standard sample

1. Introduction

Laser-induced breakdown spectroscopy (LIBS), which uses a short-pulse laser to strike the sample surface, is an elemental analysis technique that emerged in the 1960s [1]. The sample absorbs the laser energy, thereby exciting a plasma. The light emitted from the plasma is collected by a probe in the spectrometer. LIBS can be used to analyze the composition and concentrations of elements in a sample by using the plasma spectrum collected by the spectrometer [2]. LIBS exhibits several unique advantages such as a high adaptability (gas, solid, liquid) without the need for special sample treatments, preservation of physicochemical sample properties, a lower sample demand, and remote control [3]. The method has a wide range of applications in industry [4–6], military [7], agriculture [8], environmental monitoring [9], and biomedicine [10].

The generation and expansion of laser-induced plasmas involve laser–sample [11], laser–plasma [12,13], and laser–ambient gas interactions [14], which are affected by physical and chemical sample properties, laser parameters, and the ambient gas [15]. Unnikrishnan et al. [16] optimized the important parameters of ns-LIBS system and achieved good quality LIBS spectra signal for multielemental analysis. Delgado et al. [17] studied the influence of collection delay on the spectral intensity of neutral carbon atoms and CII in pyrene compounds at low pressure. It is found that the CII spectral line appears approximately 20 ns earlier than the spectral line of the neutral carbon atoms. Aragón et al.

[18] used ns-LIBS to analyze the C element in the steel under nitrogen environment, with a precision of 1.6%. Kiros et al. [19] applied ns-LIBS technology to analyze the elemental information of rocks in different climatic environments. Further, Serrano et al. [20] investigated the differences in relative intensities of spectral signatures from plasmas of several organic molecules induced in femtosecond- and nanosecond-ablation regimes. ns-LIBS is an earlier low-cost application that is suitable for the analysis of material composition and concentrations.

LIBS literature on geological-sample analysis is abundant. McMillan et al. [21] studied the geological applications of LIBS and found that spectra from four sets of rubies from Madagascar and Tanzania illustrate the use of LIBS and multivariate analysis to determine provenance with success rates higher than 95%. Pace et al. [22] used a compact LIBS system to measure spectral emission lines of Si, Al, Fe, Ca, Na, K, Mg, C, Cu, Mn, and Ti in geological samples. Moreover, Tucker et al. [23] got LIBS spectra of 100 igneous rocks at 9 m standoff distance under atmospheric Mars conditions and predicted their major elemental compositions by using partial least squares (PLS). However, the analysis of geological samples is often a challenging analytical task as it requires the determination of a large number of elements over a wide range of concentrations and in a variety of complex matrices. Clegg and Dyar et al. [24–26] used PLS to analyze the LIBS spectra, the results showed that the PLS could effectively reduce the matrix effect. In addition, the elemental fractionation effect has always seriously restricted the accuracy of analysis results. Regarding ns-LIBS technology, the laser–sample interaction is the main factor of elemental fractionation [27]. There exists a lot of literature on the effects of laser energy density, laser wavelength, laser spot size, laser pulse width, and sample matrix on the elemental fractionation [28,29]. Fryer et al. [30] first defined the elemental-fractionation index in the process of denudation. The Ca element was used as an internal standard element to standardize the elemental signals and the ratio between the latter and the first half of the denudation time. Russo et al. [31] found that the elemental-fractionation effect mainly depended on the laser energy density. Guillon et al. [32] found that the difference in the absorption coefficient of the sample material to the laser affected the distribution of the particle size of the aerosol. Kuhn et al. [33] found that filtering large-size aerosol particles produced by laser ablation could effectively reduce the elemental fractionation effect caused by ICP. However, it would cause a significant loss of instrumental sensitivity.

In this study, time-resolved photography was used to research the dynamic evolution of nanosecond-laser ablation of a geological BHVO-

* Corresponding author at: School of Mathematics and Physics, China University of Geosciences, Wuhan 430074, China.

E-mail address: lvtahn@126.com (T. Lü).

¹ These authors contributed to the work equally and should be regarded as co-first authors.

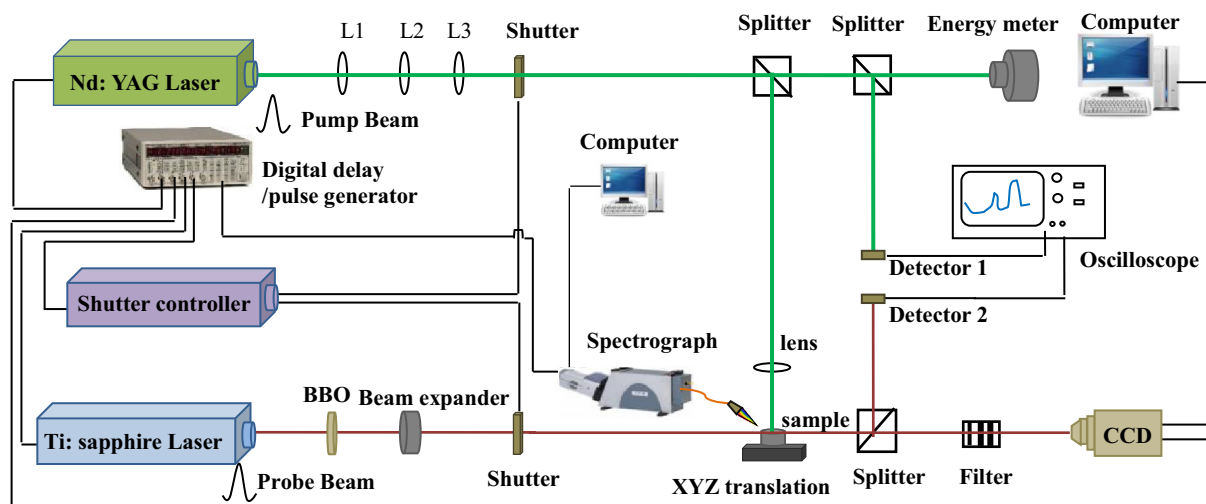


Fig. 1. Schematic of experimental LIBS setup with time-resolved photography.

2G standard sample by repeatedly analyzing the transient position of the laser-induced SW at different experimental times. Simultaneously, due to the experimental repeatability, the impact of the elemental-fractionation effect was studied via data analysis of characteristic spectra of several elements. Finally, an artificial-neural network algorithm was used to determine the Ti concentration in samples to reduce the errors caused by the fractionation effect.

2. Materials and methods

2.1. Principle of elemental determination by LIBS

The spectral line intensity of LIBS can be expressed as follows [34]:

$$I_{\lambda}^{ki} = FC_S \frac{A_{ki}g_k}{U_S(T)} e^{-E_k/k_B T}, \quad (1)$$

where I_{λ}^{ki} is the measured spectral-line intensity, C_S the elemental concentration, $U_S(T)$ the partition function, k the high-energy level of the spectral line, i the low-energy level, g_k the degeneracy of high-energy levels, A_{ki} the transition probability of characteristic spectral lines, E_k the transition energy between energy levels, T the plasma temperature, F the experimental parameter related to the efficiency of the light collection device, and k_B the Boltzmann constant. Eq. (1) indicates that the spectral-line intensity is linearly related to the elemental concentrations. Due to the influence of self-absorption, mutual interference between elements, collisional interactions within the plasma, laser-to-sample coupling efficiency and the existence of the fractionation effect, there exists a nonlinear relation between spectral line intensity and elemental concentration.

The artificial neural-network model is a mathematical model for data processing. The model uses a structure similar to neural synaptic connections [35]. It exhibits the capacity of adaptation and learning, analyzes the mapping relation of the provided input and output data, and obtains the corresponding output results. Anderson et al [36,37], separately used multilayer perceptron artificial neural networks (MLP-

ANN) and cascade correlation (CC) ANN to quantitatively analyze the LIBS spectral data of geological samples. The back-propagation artificial neural network (BP-ANN) [38–42] is primarily used for pattern recognition and classification, function approximation, and data compression and classification. Recently, the network was also applied in the field of spectral analysis and prominent results were achieved. It exhibits a considerably strong ability to solve nonlinear problems, which is suitable for the United States Geological Survey (USGS) series for standard spectral data processing.

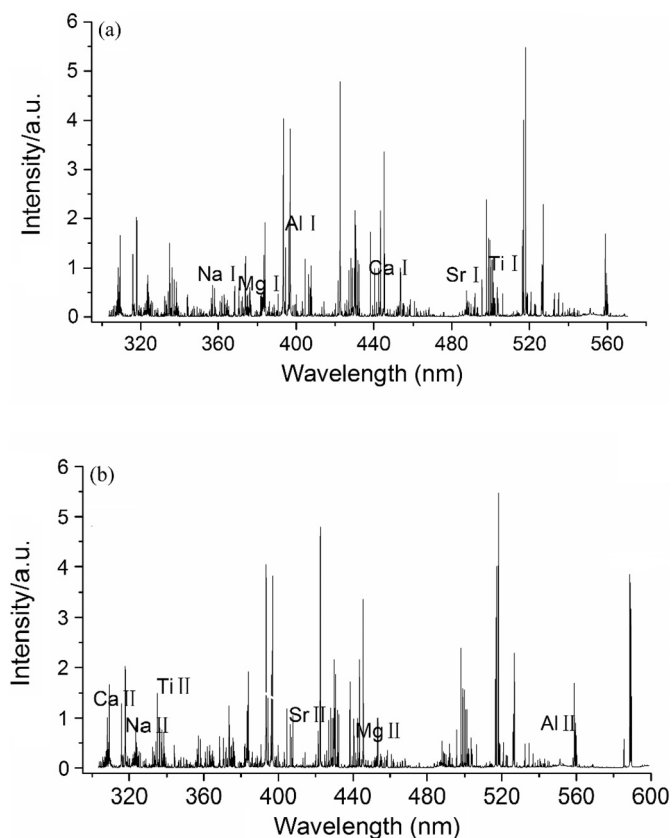


Fig. 2. Spectra of BHVO-2G covering a range of 300–600 nm. (a) Atomic spectrum; (b) Ion spectrum.

Table 1
Selected spectral lines of each element for elemental-fractionation analysis (including atomic and ion spectral lines).

Element		Sr	Ca	Mg	Al	Ti	Na
Wavelength	Atomic line	487.63	442.54	382.93	396.15	504.00	363.13
λ (nm)	Ion line	421.55	315.89	448.11	559.33	336.12	330.24

Download English Version:

<https://daneshyari.com/en/article/7673864>

Download Persian Version:

<https://daneshyari.com/article/7673864>

[Daneshyari.com](https://daneshyari.com)