



# Temporal-resolved characterization of laser-induced plasma for spectrochemical analysis of gas shales



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## ABSTRACT

Optical emission of laser ablation plasma on a shale target surface provides sensitive laser-induced breakdown spectrometry (LIBS) detection of major, minor or trace elements. An exploratory study for the characterization of the plasma induced on shale materials was carried out with the aim to trigger a crucial step towards the quantitative LIBS measurement. In this work, the experimental strategies that optimize the plasma generation on a pressed shale pellet surface are presented. The temporal evolution properties of the plasma induced by ns Nd:YAG laser pulse at the fundamental wavelength in air were investigated using time-resolved space-integrated optical emission spectroscopy. The electron density as well as the temperatures of the plasma were diagnosed as functions of the decay time for the bulk plasma analysis. In particular, the values of time-resolved atomic and ionic temperatures of shale elements, such as Fe, Mg, Ca, and Ti, were extracted from the well-known Boltzmann or Saha-Boltzmann plot method. Further comparison of these temperatures validated the local thermodynamic equilibrium (LTE) within specific interval of the delay time. In addition, the temporal behaviors of the signal-to-noise ratio of shale elements, including Si, Al, Fe, Ca, Mg, Ba, Li, Ti, K, Na, Sr, V, Cr, and Ni, revealed the coincidence of their maximum values with LIBS LTE condition in the time frame, providing practical implications for an optimized LIBS detection of shale elements. Analytical performance of LIBS was further evaluated with the linear calibration procedure for the most concerned trace elements of Sr, V, Cr, and Ni present in different shales. Their limits of detection obtained are elementally dependent and can be lower than tens of parts per million with the present LIBS experimental configurations. However, the occurrence of saturation effect for the calibration curve is still observable with the increasing trace element content, indicating that, due to the complex composition of shale materials, the omnipresent “matrix effect” is still a great challenging for the performance of quantitative LIBS measurement even in the framework of the LTE approach.

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## 1. Introduction

Mainly owing to the great interests in real-time and straightforward chemical analysis, as well as the development of commercial laser-induced breakdown spectrometry (LIBS) analytical systems, LIBS has been burgeoning as a spectroscopic technique by analyzing the spectral emissions from laser-induced plasmas. Applications of LIBS in different scientific research and industry fields have considerably grown as well over the last decade [1–4]. The basic features of this spectroscopic technique, such as to provide rapid, in situ and simultaneous multielement analysis of widespread materials with nearly free sample preparation, have been well described in the published papers [1,2,5]. These verified

versatilities allow LIBS to be an attractive and suitable analytical tool for both qualitative and quantitative elemental composition analysis of wide range geological materials either inside the laboratories or in the field [6–13]. By means of the innovative calibration-free approaches [14–17], the conventional calibration method, or advanced statistical analysis [18,19], elemental compositions of geomaterial samples can be extracted from LIBS spectra. However, as far as we know, there is very little information reported for the validation of LIBS applications for the diagnosis of unconventional hydrocarbon source rocks [20,21].

In fact, globally rising demand and consumption for hydrocarbon based products in recent years has stimulated great passions for the unconventional resources such as gas shales, coal bed gas and tight sand gas worldwide. Gas production from shales has been increasing and occupied larger proportions of the total natural gas production due to its growing output, particularly in the United States, in the last decade

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[22]. In response to these increased hydrocarbon production from shales, researches in gas and oil from low-permeability shale sequences have accelerated in many other countries as well [23–26].

Shales are enriched with various suites of major and trace elements playing decisive roles in shale gas exploration and production. Diagenetic elements like Si, Al, Fe, Ti, Ca, Mg, etc. directly correlate to the shale properties, such as porosity, gas sorption characteristics, total organic carbon (TOC) content, thermal maturity, and so on. These properties have been identified as crucial parameters for shale gas resources evaluation [27–29]. For example, as a result of the open porosity associated to the aluminosilicate fraction, total porosities can sometimes be larger in clay-rich shales compared with quartz-rich shales [27], and the mutual proportions in particular of clay and quartz appears to be a very factor related to the brittleness of shales [30], making it critical for fracture stimulation in shale gas exploration and production [31]. The conversion of organic matter and release of hydrocarbons in different organic maturation and shale diagenetic evolution history are also affected by the mineralogical compositions [32]. It was suggested that smectite, kaolinite, calcite, pyrite, and siderite greatly influence the thermal processing of oil shale formations [33]. Catalytic effects of carbonate minerals on pyrolysis reactions as well as inhibitory effects of silicate minerals were also observed in oil shales [34].

Geochemical proxies of trace elements enriched in shales are proving to be increasingly essential for revealing critical information on paleo-environmental conditions, provenance and tectonic settings [35–38]. These redox-proxying elements were delivered to the sediments in association with the organic matter under anoxic water depositional conditions [37]. Certain ones (e.g. Ti, K, Zr, Hf) have been shown to be regionally specific [35,36], and some others (e.g., Ni, V, Mo, Tl, Cd and U) can stably distribute in sedimentary strata against thermal maturation effect [37]. In recent studies, specific suites of trace element relationships, such as C–S–Fe, Ni/Co, V/Cr, Mo/Al, Re/Mo, as well as excess silica contents, have been utilized to elucidate the paleoceanographic conditions responsible for element distributions [37]. The abundances of redox sensitive trace elements (e.g. V, Cr, Mo, U, Th, Re) have also been successfully related to shale strata with increased organic paleo-productivity indicators and gas potential [37,39]. As a consequence, fast and effective definition of chemostratigraphic changes is fundamentally essential to the description and evaluation of gas-shale reservoirs.

Bulk analysis of shales in most laboratories currently relies primarily on inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF), owing to their inherent multielemental and simultaneous analytical capabilities. Although these routine approaches can accomplish the quantification analysis of elements in sedimentary rock samples accurately, the inherent problems of time-consuming sample preparation, such as grinding, wet acid decomposition in open or closed systems using ICP-OES/MS, and laborious procedures by fusion methods in XRF, impede their large routine applications in shale materials. In the case of shale-gas resources evaluation, LIBS technique can be a better alternative for rapid generation of quantitative geochemical results from shales nevertheless. Additional advantage of LIBS for in situ measurement of small areas in sub-mm or even tens of micrometer scale is especially attractive to obtaining the information of heterogeneous element distribution associated to mineralogy features in shale lamina. The sensitive surface mapping by LIBS of a number of major and minor elements in shale has been demonstrated in our previous work [40]. However, rather detailed analysis of the plasma induced on shale targets is still necessary in order to optimize the experimental program for the generation of plasmas with suitable properties for LIBS measurement. Despite a few studies carried out for the plasmas induced from metallic as well as non-metallic samples (such as biological samples) with the aim to verify the validity of the local thermodynamic equilibrium (LTE) under typical ablation conditions [41,42], characteristics of laser-induced plasma from shale are still unknown. The result of

such an investigation will raise the plasma characteristic dependence on the ablation conditions as well as the temporal evolution of plasma expansion and decay. This is a crucial step towards the quantitative LIBS measurement of shales.

The purpose of this work is to determine and discuss the experimental conditions which are most suitable for routine spectrochemical analysis of shales by LIBS. We present the resulted different characteristics of the plasma induced on a pressed pellet sample of powdered typical shale with ns Nd:YAG laser pulses in air. With the experimental protocol described in this paper, time-resolved and space-integrated plasma emissions are measured for different laser fluencies. The physical parameters of the plasma, including electron density, the atomic and ionic temperatures, are retrieved from spectroscopic diagnostics based on Stark broadening, Boltzmann plot (BP) and Saha–Boltzmann plot (SBP) method for the validation of the LTE towards the plasmas induced from the shale pellet surface. To further examine and optimize the analytical performance of laser pulse impact on shale pellet, temporal evolution of the signal-to-noise ratios (SNRs) for different elements were also studied. The results of the temporal behavior of the SNRs demonstrate an accordance of a certain time window during which the induced shale plasmas are in LTE. Desirable LIBS measurement could be well obtained with such conditions. We finally described the calibration curves and the content limit of detections (LODs) of the concerned trace elements detected in different shale samples with our LIBS procedure, including Strontium, Vanadium, Chromium and Nickel. The noticeable saturation effect for the calibration curves with the increasing trace element content indicates the ubiquitous “matrix effect” owing to the complex composition of shales.

## 2. Experimental

A Nd:YAG laser delivering a laser pulse of 4–7 ns FWHM at fundamental wavelength (Litron, 1064 nm) was used in the experiment. Laser pulses were aligned and perpendicularly focused on the pressed shale sample surface using a bi-convex quartz lens with a 15 cm focal length. Different laser pulse energies of 45 mJ, 65 mJ, and 85 mJ were used in this work. To improve the reproducibility of the laser-induced micro-plasma, the focus plane of the lens was set nearly 5 mm under the pellet sample surface. The focused spot size on the sample surface was estimated to be about 700  $\mu\text{m}$  in diameter by microscopic pictures of ablation craters, resulting in estimated laser irradiance on the pellet surface of  $1.95 \times 10^9$ ,  $2.82 \times 10^9$ , and  $3.68 \times 10^9$   $\text{W}/\text{cm}^2$ , respectively.

With respect to the collection optics, an attached quartz collimating lens (Avantes UV-74) was held on a stage at an accident angle of  $45^\circ$  to the target surface for collimating the optical emission from the plasma into a coupling fiber (400  $\mu\text{m}$  core diameter). The fiber was connected to an echelle spectrometer (LTB; spectral range: 220 nm to 800 nm; spectral resolution:  $\lambda/\Delta\lambda = 9000$ ) with a coupled ICCD camera (iStar from Andor Technology). The wavelength calibration of the spectrometer and spectral response of the detection system were respectively performed with its mercury argon lamp and a certified deuterium halogen tungsten light source (Avalight-DH-BAL-CAL from Avantes) prior to the experiment. This is necessary for a valid calculation of the plasma temperature by LIBS spectroscopy as well as for an estimation of plasma compositions by calibration method.

Typical black shale samples came from Sichuan basin, China. As detailed described in our previous published work [40], the shale samples were prepared with a grain size of 200 mesh sieve (74  $\mu\text{m}$ ) and pressed by 25 tons of hydraulic machines into 32 mm diameter by 3 mm thick pellets. The optical signal of the plasma plume induced on the pellet surface was then sent to the echelle spectrometer. For time-resolved detections of the plasma emission, the spectral acquisition by the ICCD camera was synchronized to the Q-switch trigger of the laser. Prior to a detection window opened for the camera, a delay time is necessary to avoid the strong continuum emission immediately after the impact of the laser pulse on the pellet surface. In order to compensate for the

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