Analytical Note

# Laser Induced Breakdown Spectroscopy of meteorites as a probe of the early solar system ☆

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ABSTRACT

This paper presents an evaluation of Laser Induced Breakdown Spectroscopy (LIBS) as a technique for gathering data relevant to Solar System geophysics. Two test cases were demonstrated: elemental analysis of chondrules in a chondrite meteorite, and space- resolved analysis of the interface between kamacite and taenite crystals in an octahedrite iron meteorite. In particular most major and minor elements (Fe, Mg, Si, Ti, Al, Cr, Mn, Ca, Fe, Ni, Co) in Sahara 98222 (chondrite) and its chondrules, as well as the profile of Ni content in Toluca (iron meteorite), were determined with the Calibration Free (CF) method. A special attention was devoted to exploring the possibilities offered by variants of the basic technique, such as the use of Fe I Boltzmann distribution as an intensity calibration method of the spectroscopic system, and the use of spatially resolved analysis.

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## 1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) has been proved a powerful tool for space application thanks to its versatility, robustness, and, more relevant to this field, remote sensing capabilities, compactable setup, and no need of direct contact with sample and polishing of its surface [1]. LIBS has already been employed for Mars exploration in the ChemCam instrument mounted on the NASA "Curiosity" rover [2], and in a near future it may be possible to exploit it for on flight exploration of minor bodies, such as asteroids or human debris. In particular, the chemical composition of asteroids may provide important information about the solar system and the universe [3,4]. Among the advantages mentioned above, and thanks to the laser induced plasma peculiarities [5], LIBS allows performing elemental analysis without standard samples, by Calibration Free (CF) methods, thus enhancing the capabilities of measurements in extreme conditions [6].

As an analytical method, CF-LIBS has been applied recently to the analysis of meteorites [7,8], which has suggested that this technique is far beyond its benchmarking stage and can play a precious role in astrochemistry and space geophysics. This statement is further demonstrated in this work by using two test cases, relevant to obtain data related to the early evolution of solar system matter. The first test case, which

applies to stony meteorites, is the chemical identification of chondrules embedded in a chondrite meteorite. Condrules are primordial solar matter formed in the early nebula even before the development of asteroids, as a consequence of local gaskinetic cooling [9]. They are formed by minerals with very high sublimation temperature, which appear in the highest region of the so-called condensation sequence [10] and start to solidify earlier than the more volatile minerals, which constitute the matrix matter between chondrules. These tiny spherules, with a typical diameter in the range of 0.1–10 mm, represent therefore pristine early matter and date back to about 4.6 billion years, older than the oldest available Earth rocks. As a consequence, they contain the most primitive matter available for direct analysis [10]. The second test case demonstrated here applies to iron meteoroids, and precisely to Fe–Ni octahedrites. These display the so-called Widmanstätten features (described in details later on), whose microprobe analysis, combined with theoretical considerations, allows estimating the radii of the parent bodies of these meteorites [11], and thereby providing indirect experimental data to evaluate planetesimal accretion models for the formation of planets [3].

From the analytical point of view, in this work CF-LIBS was applied to the elemental analysis of Sahara 98222 (L6 chondrite) and its chondrules, to quantify Fe, Mg, Si, Ti, Al, Cr, Mn, Ca, Fe, Ni and Co contents, and for tracking the Ni content profile across the Widmanstätten structure of Toluca (iron meteorite). Furthermore, with the idea of minimizing any possible calibration procedures, the intensity calibration of different spectral ranges with a radiometric lamp was avoided by using a calibration based on Boltzmann distribution of one of the elements present in the sample.

## 2. First test case: chemical composition of chondrites and chondrules

Chondrites, the most common type of stony meteorites, are considered to have the same composition and origin of the solar system, since they date back to the age of the solar system formation (i.e. 4.6 Ma) and their contents of non-volatile elements are close to those in the solar photosphere. Chondrites have mainly ultramafic composition, largely consisting of Fe, Mg, Si and O. Their main constituents are the chondrules, and their bulk composition contains different proportions of refractory inclusions (Ca- and Al-rich), metallic inclusions (Fe, Ni), and material matrix (grains of volatile materials that fill all the interstices).

Chondrules are igneous particles formed after the solidification of molten silicate masses containing various components, later incorporated into meteorite parent bodies. Chondrules are roughly millimeter-sized particles that crystallized in minutes to hours, at temperatures between 1800 and 1300 K, from the least volatile components of primordial gases prior to accretion. They are largely composed of olivine and pyroxene, with metallic (Fe and Ni) grains, often clustered near the periphery. As [4,9,12] indicate, the study of chondrites and in particular of their chondrules is important to retrieve information on the accreted mass in the inner solar system and suggests that chondrule formation may have been the process that triggered accretion in the solar nebula. Therefore, since Wood [9] first proposed this hypothesis, many studies have been and are still being made, in order to understand the initial accretion processes in the solar nebula through the chondrules texture and composition.

Due to its characteristics as an analytical technique, LIBS can be employed to reveal substantial differences between the elemental composition of chondrite bulk and chondrules and thus it can effectively complement well-established analytical techniques generally used in this field, such as electron microprobe [13] and ion probe analysis [14] and INAA [15].

The chondrite analyzed in this work is an L6 ordinary chondrite (Sahara 98222). A chemical composition comparison between bulk chondrite and two of its chondrules was performed based on the quantification of major and minor elements.

### 2.1. Experimental setup and procedures

The employed experimental setup is described in details in ref. [7,8], where the Calibration Free (CF) procedure was used to determine the elemental composition of a large number of meteorites.

The experimental setup consists of an Nd:YAG pulsed laser with a time duration of 7 ns and a repetition rate of 10 Hz, operated at its second harmonic (532 nm). The spectroscopic system consists of a Czerny–Turner monochromator (TRIAX 550 Jobin Yvon) with 1800 g/mm grating, an ICCD (i3000 Jobin Yvon) and a pulse generator (Stanford Inc. DG 535) for selecting the delay time and the gate width of the detector. The radiation emitted by the plasma is focused through a 7.5 cm focal length biconvex lens directly on the monochromator slit.

The sample was cut in two parts to analyze the interior of the meteorite and avoid the analysis of crust. A bulk chondrite measurement was performed by rotating the target, so to obtain an average element concentration of the chondrite over as large as possible an area. Then, after identifying a pair of chondrules (as shown in Fig. 1), the meteorite was kept fixed and the laser was focused (spot diameter 150 μm) on each chondrule (sizes around 600 ± 200 μm). Every emission spectrum was acquired by averaging a number of accumulations, so as to optimize the signal-to-noise ratio and overcome problems linked to the sample heterogeneity and to the use of multiple spectral windows. With the employed Czerny–Turner monochromator, a 16 nm spectral window can be acquired at a time; thus, seven spectral ranges had to be acquired to ensure the detection of all the elements in the sample. As an example, the emission spectra of bulk chondrite are shown in Fig. 2 in 6 acquired spectral windows (the 5th spectral region is not it isn't shown because it is overlapped by the 6th one). Time delay and gate width were 800 ns
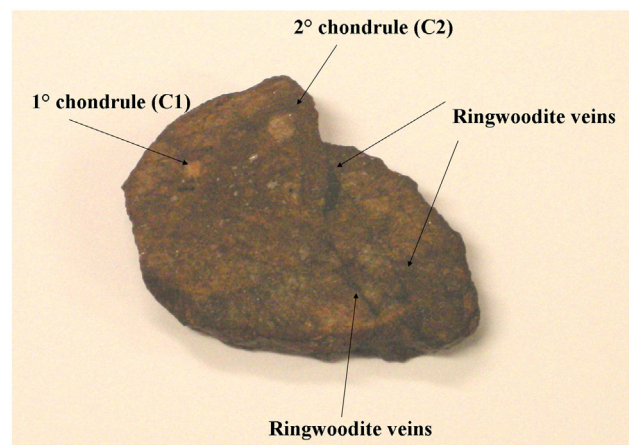


**Fig. 1.** Picture of a slab of Sahara 98222 (chondrite meteorite). The two embedded chondrules (C1 and C2) are clearly visible.

and 5 μs respectively and the laser energy was 16 mJ. Table 1 shows the chosen atomic emission lines of the detected elements. The emission lines of Fe I were used to draw the Boltzmann plot and determine the excitation temperature ($T_{ex}$) for each measurement. Electron number density ($N_e$) was determined through the Stark broadening of Ni I (341.47 nm) [16], in order to calculate the ionized fraction of each element. The obtained $T_{ex}$ and $N_e$ values for the chondrite bulk and the two chondrules are reported in Table 2.

Fe, Mg, Si, Ti, Al, Cr, Mn, Ca, Fe, Ni, and Co were quantified in the bulk chondrite and in the two embedded chondrules, with the CF method described in details in refs [7,8]. The normalization procedure for the CF method to obtain the weight percentage of each element was made without taking into account the amount of Na, S and P. The emission lines of Na I heavily suffer from self-absorption and S I and P I emission lines are not clearly detected because of the strong interference with the iron emission lines. For this reason the normalization was forced to 97% instead of 100%. If a 100% normalization is performed (as is usual with unknown samples), uncertainties on the elemental composition increase by 3% for each element (with respect to those reported in this paper with the 97% normalization). In other words, the uncertainties increase because the percentage of the undetectable elements is re-distributed in the calculated percentages of the others. As for the oxygen content, which is not directly measurable in experiments performed in air, it was calculated by the stoichiometric relation in the mineral oxides of the detected metals.

Finally, to apply a CF multi-elemental analysis with a Czerny–Turner monochromator, several spectral windows are usually acquired; thus, an intensity calibration procedure is needed to account for the different instrumental efficiency (monochromator and ICCD) at different spectral windows. Usually this spectral window calibration is carried out with a radiometric lamp. To avoid the use of radiometric sources and at the same time to normalize any differences in the LIPs (i.e. each acquired spectral window corresponds to a different LIP event), a normalization procedure based on the Fe I Boltzmann distribution was followed here. Fe was chosen because it is found in all meteorite classes and because of its large number of emission lines in the UV–vis spectral range.

In each acquired spectral window, in addition to the emission lines of the elements to be analyzed, a certain number of Fe I emission lines was selected (Table 3). After the determination of the excitation temperature from a Boltzmann plot drawn with the Fe I emission lines of a single spectral window (in this case the third of Table 3), the intensity of each other Fe I emission line, was calculated by the fitted equation of the Boltzmann plot:

$$\ln\left(\frac{I_{calculated}^{FeI} \cdot 4\pi}{A_{iu}h\nu_{iu}g_u}\right) = -\frac{E_u}{kT_{ex}} + \ln\left(\frac{N_{0,FeI}}{Z(T)}\right) \tag{1}$$