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Laser-Induced Breakdown Spectroscopy (LIBS) Potential for Carbon Detection in Stony Meteorites

O. DE PASCALE[1] – P. MANZARI[2] – B. MARANGONI[3] – G. NICOLODELLI[3]
G.S. SENESI[1]*

[1] CNR - Istituto per la Scienza e Tecnologia dei Plasmi (ISTP) – Sede di Bari, Via Amendola 122/D, 70126, Bari, Italy.
[2] Agenzia Spaziale Italiana, via del Politecnico, 00133, Roma, Italy.
[3] Physics Institute, Federal University of Mato Grosso do Sul, P.O. Box 549, Campo Grande, MS 79070-900, Brazil.
* Corresponding author: giorgio.senesi@cnr.it

Abstract – The detection and spatial localization of carbon in meteorites are very important as carbon bearing minerals can reveal the history of their parent bodies. The analysis of free carbon in meteorites is usually performed by techniques either destructive or implying sample preparation. More recently, a slightly destructive technique not requiring any preparation procedure, i.e. Laser-Induced Breakdown Spectroscopy (LIBS), has been used for the preliminary qualitative and quantitative elemental analysis of meteorites of different nature and origin. In this study, a few examples of LIBS application to carbon analysis in some representative meteorite samples are described.

Keywords: Laser-Induced Breakdown Spectroscopy; LIBS; meteorite; carbon; chondrite

Riassunto – La rilevazione e la localizzazione spaziale del carbonio nei meteoriti sono molto importanti in quanto i minerali che contengono carbonio possono rivelare la storia dei loro corpi originari. L'analisi del carbonio libero nei meteoriti viene di solito eseguita mediante tecniche distruttive o che implicano la preparazione del campione. Più recentemente, una tecnica leggermente distruttiva che non richiede alcuna procedura di preparazione, cioè la spettroscopia di rottura indotta da laser (LIBS), è stata utilizzata per un'analisi elementare preliminare di tipo qualitativo e quantitativo su meteoriti di diversa natura e origine. In questo studio, sono descritti alcuni esempi di applicazione della LIBS per l'analisi del carbonio in alcuni campioni rappresentativi di meteoriti.

Parole chiave: Spettroscopia di rottura indotta da laser; LIBS; meteorite; carbonio; condrite

Introduction

The investigation of carbon forms and distribution in chondrites can contribute better than most other elements to understanding the early stages of solar system formation due to the sensitivity of this element to chemical and physical conditions that prevailed in that situation. Although carbon has been

widely investigated in carbonaceous chondrites, and special forms, such as diamond and silicon carbide have been recognized in some chondrites, the spatial distribution and nature of carbon in ordinary chondrites have received much less attention due to their lower carbon content and the difficulties to determine this element at low concentrations. In particular, a median value measured of 0.1 wt% of bulk carbon, which decreased with increasing the petrologic type, measured in ordinary chondrites [1]. The largest value of 0.95% was measured in the H3 chondrite Sharps, whereas the smallest one of 0.016% was found in the H5 chondrite Allegan [1,2]. Fredriksson *et al.* [3] and Makjanic *et al.* [4] suggested that most carbon occurred in the chondrite "matrix". Successively, the finding of graphite-magnetite aggregates [5] and of poorly graphitized and/or amorphous carbon in aggregates with Ni-Fe [6] confirmed complexity of this issue. Further, systematic studies of the spatial distribution and structural forms of carbon in the Allende meteorite showed that this element was present mainly as greatly disordered graphitic forms mostly in spaces between chondrules and inclusions [7-10]. This form of carbon was also previously found to occur as rimming chondrules in some unequilibrated ordinary chondrites [11].

The detection and quantification of free carbon in meteorites have been commonly performed by either destructive techniques, including Total Organic Carbon and Inductively Coupled Plasma Mass Spectrometry, or by techniques implying sample preparation, such as Scanning Electron Microscopy using Au to coat the sample surface, whereas vibrational spectroscopies such as Infrared and Raman are generally used to analyse carbon compounds. Further, Laser-Induced Breakdown Spectroscopy (LIBS) has been used to achieve preliminary results on the qualitative and quantitative composition of meteorite samples of different nature and origin [12,13]. Differently from other techniques, LIBS is able to detect both elemental and combined carbon even at ppm levels on the whole fragment or petrographic thin sections of a meteorite.

In this study, the qualitative carbon analysis will be performed and discussed on petrologic matrices of ordinary chondrites of subgroups H and L, an achondrite, and a meteor-wrong for comparison.

Materials

Four meteorite samples (Fig. 1) were examined: (i) three stony meteorites consisting of two ordinary chondrites of the H3 type, both as a whole bulk fragment and petrographic thin sections, and a not classified L3 type collected in the Bouarfa area (Morocco); and (ii) the classified eucrite (achondrite) named Northwest Africa (NWA) 4051, which was found in 2004 in the Kem Kem Basin, Algeria [14]. This meteorite consisted of large pyroxene and plagioclase grains of composition ranging, respectively, from pigeonite to subcalcic augite and essentially anorthite, in a matrix of the same mineral composition but smaller grain size with minor phases including oxides such as chromite, ilmenite, silica, iron sulfide and a Ni-rich metal Fe-phase. Further, one industrial carbon-bearing pig-iron sample, which is an intermediate product of the iron industry and the basic ingredient before further processing to produce steel, was used as a standard for C content to be compared to meteorite samples. This kind of samples, also known as meteor-wrongs, are sometimes identified visually and classified erroneously in the field as iron meteorites.

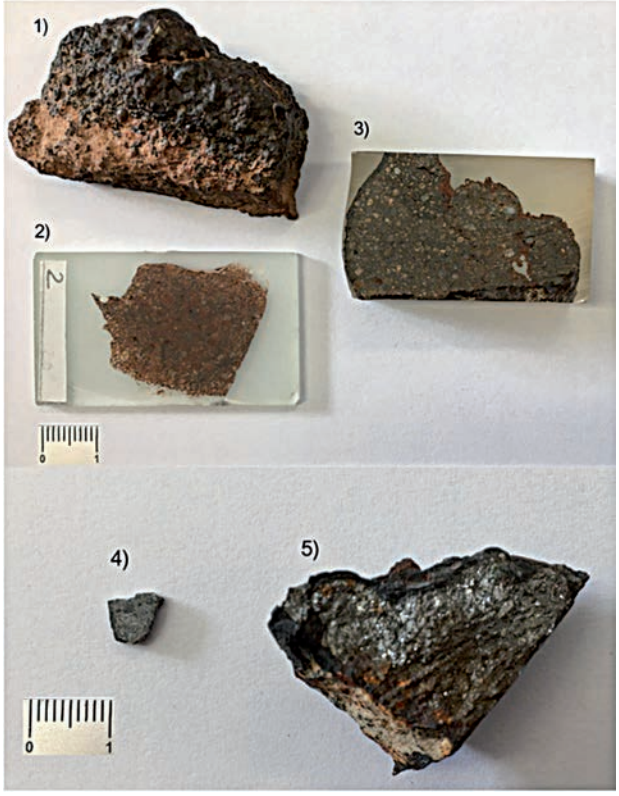

Fig. 1. Images of (1) a fragment of the whole meteorite chondrite H3 and (2) of a thin petrographic section cut from it; (3) a fragment of the whole meteorite chondrite L3; (4) a fragment of the whole meteorite NWA 4051 and (5) a suspected meteorite named "meteor-wrong".

Methods

The LIBS system was composed of a Nd:YAG Q-switched laser operating at 1064 nm wavelength with 6 ns pulse duration and maximum energy of 200 mJ per pulse (Fig. 2). The beam was focused on the sample in a 50- m spot diameter, resulting in a power density of approximately 2×1012 W/cm^2. The plasma light was captured by a Stellarnet spectrometer operating in the spectral range of 190-300 nm with a 0.2 nm optical resolution. The delay time between the laser shot and spectra acquisition was 500 ns. A total of 10 measurements were performed in atmospheric ambient on each sample without no pre-preparation by exploring its surface at different positions and accumulating 2 shots at each of them, finally obtaining one averaged spectrum for each shot.

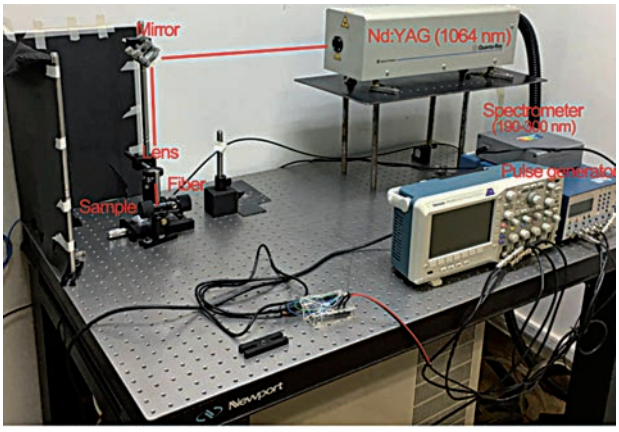

Fig. 2. LIBS experimental set-up.

Results and Discussion

Effect of the laser beam

The surface morphology of the craters formed after 2 laser shots was investigated by optical microscopy. Images obtained (Fig. 3) indicated that the energy density used was sufficient to provide sample ablation and crater formation only after two laser shots. Further, Fig. 3 shows that the laser-impacted area could be divided into a central intensely ablated region and a rim around it where the material re-solidified in the form of droplets and cracks. Some black spots could be also observed with pinholes appearing on the surface, and size of holes ranging from several hundreds of nanometers up to a few microns. A number of cracks could also be observed, which might be due to the rapid temperature change in response of laser irradiation. Further, the surface color changed to black and the surface reflectivity decreased significantly. The crater diameters after laser shots was estimated about 300 μm (Fig. 3).

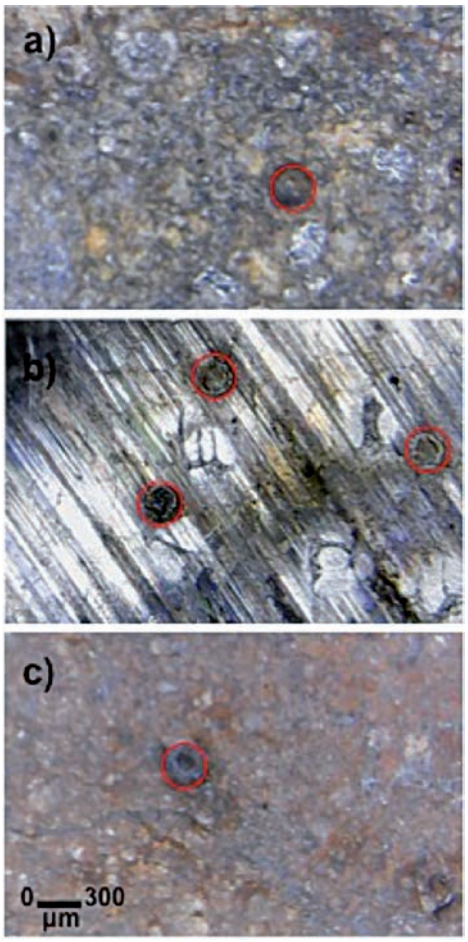

Fig. 3. Images of laser beam craters (red circles) obtained on (a) a fragment of the whole meteorite chondrite L3; (b) a suspected meteorite named "meteor-wrong" and (c) a thin petrographic section of the meteorite chondrite H3.

Qualitative LIBS analysis

The preliminary qualitative analysis of LIBS emission spectra measured on the five samples in the spectral range 180-300 nm (Fig. 4) shows that the main elemental components of the meteorites were Co, Fe, Mg, Si and Ti, whose emission lines are listed in Table 1. An intensity variation of Fe, Mg and Si peaks among the samples was verified qualitatively in the LIBS spectra acquired (Fig. 3) which reflected distinct chondrite features. Based on the contents of free metals, mainly Fe, the letter "H" was associated to values around 20% of the mass and letter "L" to values around 10% [15]. Further, Mg and Si are the major constituents of olivine

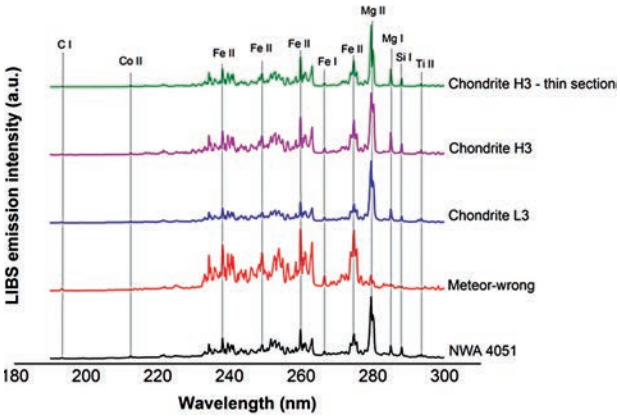

Fig. 4. LIBS spectra acquired in the range 180-300 nm on the chondrite H3 meteorite, both thin petrographic section and bulk fragment, the chondrite L3 meteorite, the meteor-wrong sample, and the achondrite NWA 4051.

mineral that is one of the main components of these classes and almost all chondritic meteorites and the first major Mg-silicate phase to condense from cooling solar nebula. Further, the possible occurrence of carbon in olivine, either as dissolved element in the structure or in the form of carbonaceous phases, i.e. graphite, silicon carbide and other compounds, even as sub-microscopic bubbles, is of fundamental importance for the knowledge of the physico-chemical conditions existing during the early stage of chondrule and pre-chondritic matter formation [16].

Table 1. Spectroscopic atomic emission lines (NIST, KURUCZ) of samples examined.

Element	Wavelength (nm)
Co II	212.50
Fe II	234.41; 235.91; 238.20; 248.94; 259.93; 261.18; 266.25; 273.95; 274.91; 275.57
Si I	288.17; 251.61; 251.92
C I	193.09
Ti II	293.59
Mg I	285.21
Mg II	279.55; 280.27

All the spectra featured an intense background, especially in the wavelength range 230-270 nm where multiple lines of the major matrix element, Fe, appeared. Due to the dominant presence of Fe lines in all the spectra, the main differences among them could be revealed only examining in further detail the entire spectral range (Fig. 4). In particular, the specific signals of the elements Mg I (at 285.21 nm) and Si I (at 288.17 nm) were evident in true meteorites spectra, but not in that of the meteor-wrong sample.

The spectral window where the emission lines of atomic C at 193.03 and at 247.86 nm appeared (Fig. 5) was used first for qualitative analysis and then to quantify C in the samples. As the meteorite samples under study are rich in Fe, its lines prevented to correctly identify and quantify C using the line at 247.86 nm, unless a proper correction was applied to eliminate, or at least reduce Fe interferences (mainly the Fe line at 247.94 nm). Differently, the C line at 193.03 nm was not interfered by other elemental emission lines and could be spectrally resolved by LIBS. In particular, Fig. 5 shows the LIBS emission spectra of the C line at 193.03 nm for the meteor-wrong sample (red line), the achondrite NWA 4051 (black line), the chondrite L3 (blue line), and the chondrite H3 bulk sample (purple line) and its thin petrographic section (green line).

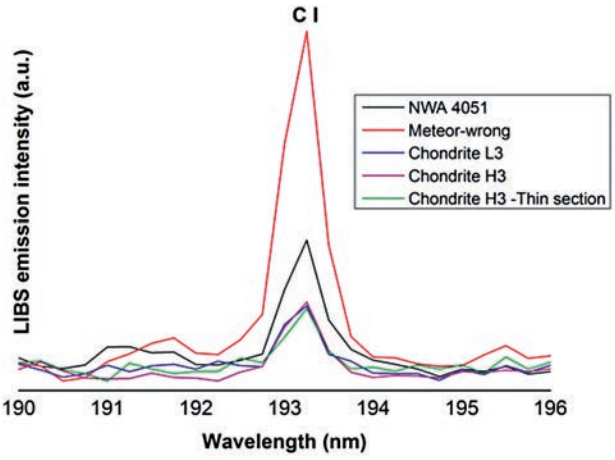

Fig. 5. LIBS spectra acquired in the range 190-196 nm showimg the C line at 193.03 nm in the meteor-wrong sample (red line), the achondrite NWA 4051 (black line), the chondrite L3 (blue line), the chondrite H3 bulk sample (purple line) and its thin petrographic section (green line).

However, LIBS analysis could not reveal the chemical state nor the crystalline structure of the element C in meteorites. Thus, only when further chemical and structural information will be available, appropriate assignments to specific C forms in meteorites, such as graphite, disordered graphite, diamond, soot, silicon carbide, etc. could be made by LIBS.

Conclusions

The preliminary results achieved in this work show the potential of LIBS for revealing differences in the

spectral emission line of C in different meteorites in comparison to a meteor-wrong sample. The LIBS technique features various advantages over other analytical techniques, such as the capacity to detect down to ppm of carbon and no requirement of any sample manipulation or preparation. Further LIBS analyses of additional samples will be performed and validated using other standard techniques to identify the carbon-bearing phases and draw calibration curves for each meteorite group.

REFERENCES

[1] Dood R.T. JR., Van Schmus W.R., Koffmand D.M. (1967). "A survey of the unequilibrated ordinary chondrites." Geochimica et Cosmochimica Acta. 31. 921-951.

[2] Moore C.B. and Lewis C.F. (1967). "Total carbon content of ordinary chondrites." Journal of Geophysical Research. 72. 6289-6292.

[3] Fredriksson K. Jarosewich E., Nelen J. (1969). The Sharps chondrite-New evidence on the origin of chondrules and chondrites. In: Meteorite Research (ed. P. M. Millman), pp. 155-165. Springer- Verlag, New York.

[4] Makjanic J., Vis R.D., Hovenier J.W., Heymann D. (1993). "Carbon in the matrices of ordinary chondrites." Meteoritics. 28. 63-70.

[5] Scott E.R.D., Taylor G.J., Rubin A.E., Obada A., Keil K. (198l). "Graphite-magnetite aggregates in ordinary chondritic meteorites." Nature. 291. 544-546.

[6] Brearley A.J. (1990). "Carbon-rich aggregates in type 3 ordinary chondrites: Characterization, origins, and thermal history." Geochimica et Cosmochimica Acta. 54. 831-850.

[7] Van der Stap C.C.A.H., Vis R.D., Verheul H., Heymann D. (1985). "Spatial distribution of carbon in the Allende meteorite and possible origin of his elusiveness." Meteoritics. 20. 761.

[8] Heymann D., Vis R.D., Van der Stap C.C.A.H. (1985). "Carbon concentration mapping in a surface of the Allende meteorite." Proc. Lunar Planet. Sci. 16th 348-349.

[9] Heymann D., Makjanic J., Van der Stap C.C.A.H., Vis R.D., Verheul H. (1988). Carbon; oxygen, silicon, sulphur, calcium, and iron determinations in 24 dark clasts and one dark inclusion of the Allende meteorite by $^{12}C(d,p)^{13}C$ nuclear reaction and PIXE. Meteoritics. 23. 131-137.

[10] Heymann D. and Read N. (1987). "Raman study of carbon in Allende." Proc. Lunar Planet. Sci. 18th, 423-424.

[11] Michel-Levy M.C. and Lautie A. (1981). "Microanalysis by Raman spectroscopy of carbon in the Tieschitz chondrite." Nature. 292. 321-322.

[12] Senesi G.S. (2014). "Laser-Induced Breakdown Spectroscopy (LIBS) applied to terrestrial and extraterrestrial analogue geomaterials with emphasis to minerals and rocks." Earth-Science Reviews. 139. 231-267.

[13] Senesi G.S., Capitelli F. (2019). "Compositional, mineralogical and structural investigation of meteorites by XRD and LIBS." Chapter in book "Hypersonic Meteoroid Entry Physics", ed. by G. Colonna, M. Capitelli and A. Larucchiuta, IOP Series in Plasma Physics.

[14] Connolly H.C. Jr., Zipfel J., Folco L., Smith C., Jones R.H., Benedix G., Righter K., Yamaguchi A., Chennaoui Aoudjehane H., Grossman J.N., (2007). "The Meteoritical Bulletin, No. 91, 2007 March." Meteoritics & Planetary Science. 42. 413-466.

[15] M.K., Weisberg, T.J. McCoy and A.N. Krot, Systematics and evaluation of meteorite classification, in: D.S. Lauretta and H.Y. McSween Jr. (Eds.), Meteorites and the Early Solar System. University of Arizona Press, Tucson, 2006, pp. 19-52.

[16] Varela M.E., Métrich N. (2000). "Carbon in olivines of chondritic meteorites." Geochimica et Cosmochimica Acta. 64. 3433-3438.