

ChemCam LIBS: A Powerful Tool for Textural Comparison of the DAG 476 Meteorite and Picritic Basalt. A. Cousin¹, V. Sautter², C. Fabre³, S. Maurice¹, R. Wiens⁴, ¹Institut de Recherche en Astrophysique et Planétologie, Toulouse (agnes.cousin@irap.omp.eu), ²Muséum National d'Histoire Naturelle, Paris, ³G2R, Nancy Université, ⁴Los Alamos National Laboratory, New Mexico.

Introduction: ChemCam is part of the Mars Science Laboratory (MSL) rover payload, launched the 26th November 2011. This instrument uses the Laser-Induced Breakdown Spectroscopy (LIBS) technique to investigate the chemistry of the martian surface [1,2]. ChemCam (Chemistry Camera) is composed of the Body Unit (located in the body of the rover), including the spectrometers, the Mast Unit including the laser, the Remote Micro Imager (RMI), the telescope and their electronics.

ChemCam will be the first instrument using the LIBS technique for planetary studies, performing analyses at remote distances from 1 to 7 meters. As the spatial resolution of this instrument is a few hundred microns, each burst will analyze individual or a few coexisting minerals that may not represent the whole-rock composition. The RMI coupled with the LIBS on the rover mast has an angular resolution of $\sim 100 \mu\text{rad}$, permitting the observation at 3 m of crystals $300 \mu\text{m}$ dia. [3]. It precludes remote identification of smaller crystals (with size much less than a millimeter). Thus, ChemCam optical measurements will be blind for fine-grained textured rock such as basaltic rocks encountered so far on Mars at Gusev crater, like the Adirondack class of rocks [4].

The objective of this work is to test the capability of ChemCam to rapidly distinguish rocks displaying different grain size distributions. The aim of this study is to provide simple tools for future first-order interpretations of LIBS data during the MSL operations.

Samples: Three samples were specially selected: (i) a terrestrial analogue of Adirondack rock, the picrite hotspot-related basalt from shield volcano of La Reunion island (Indian Ocean), (ii) a coarse-grained picritic shergottite DaG 476, and (iii) a synthetic glassy target of picritic composition with micron sized microliths [5]. We aim to gain experience regarding compositional and textural information that can be obtained on key igneous mineral groups such as olivine, plagioclase and pyroxene using in situ LIBS analyses.

Experimental Setups: The scanning electron microscope (SEM) is a TESCAN VEGA II LSU. It was used to characterize the polished section after laser ablation. It is equipped with a Back-Scattered Electron (BSE) detector for imaging and an Energy Dispersive X-ray Spectrometer for chemical analyses. The SEM observations and the EDS analyses were performed in high vacuum mode with an accelerating voltage of 15kV and at a working distance of 16.2 mm.

The LIBS analysis were performed in Toulouse, at IRAP, using the EQM (Engineering and Qualification Model) for the Mast Unit and commercial spectrometers for the Body Unit. Samples were placed at 3 m in a chamber simulating the Martian atmosphere (composition and pressure, [6]). Five bursts accumulating 10 laser shots were randomly performed on each target at blind conditions in order to sample five different locations representative of the whole rock composition.

Results: The first objective is to check if the 5 bursts were done in the matrix or in a phenocryst. Only 5 LIBS spectra are acquired for each sample, and we compared each of them to check some possible emission lines ratios changes. The picrite basalt does not show significant variations of the various LIBS emission lines. The plasma seems thus to be representative of the same mineral mixture, as opposed to DaG 476 spectra the second spectrum of which presents higher Mg emission lines (fig.1). As these samples are olivine-rich phenocryst rocks, we focused on the Mg/Si ratio, using the Mg line at 285.88 nm and the Si line at 288.18 nm. The Mg/Si ratios typically obtained on olivines (here, San Carlos olivine, [7]) are always higher than 1.6. In the picrite basalt, the ratios obtained are always below 1.6 (the mean is 0.8), whereas on the DaG 476, one spectrum (fig.1) presents a Mg/Si ratio of 1.8, almost characteristic of an olivine crystal LIBS signal. The BSE analysis confirmed this observation. To exclude the spectrum from the phenocrysts, as the objective is to compare the matrix signal, only the four other spectra from the DaG 476 were averaged, whereas the five from the picrite basalt were averaged.

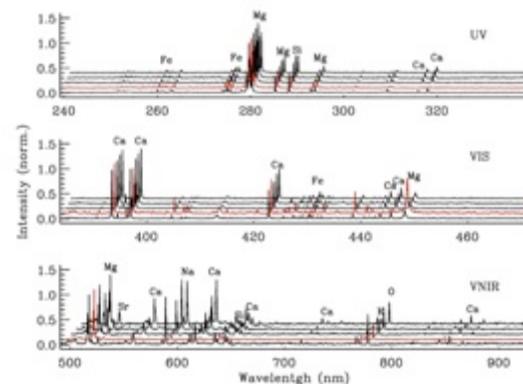


Figure 1 : Spectra on DaG 476 sample, on 5 different locations.

The subtraction of these two mean spectra (DaG 476 and picrite basalt) displays chemical differences essentially for the alkali and aluminum content: the shergottite

meteorite is alkali feldspar-depleted, with Al, Na and K emission lines presented as negative on figure 2. Some other lines ratios were also tested to further constrain chemical and mineralogical differences between these two matrices. The emission lines used are : Na at 589.15 nm, K at 766.70 nm, Si at 634.88 nm, Ca at 616.38 nm, Al line at 308.31 nm, and Mg at 518.5 nm.

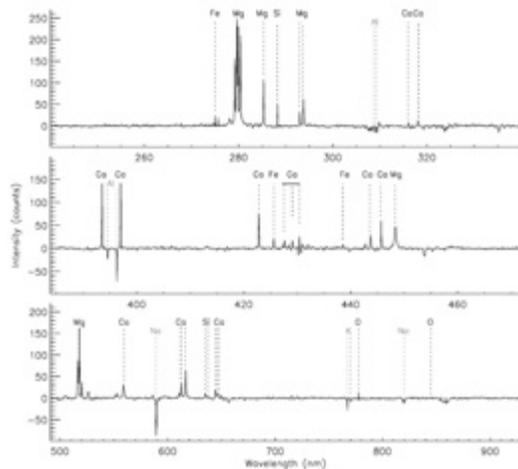


Figure 2 : Substraction of the picritic basalt mean spectrum to the DaG 476 mean spectrum.

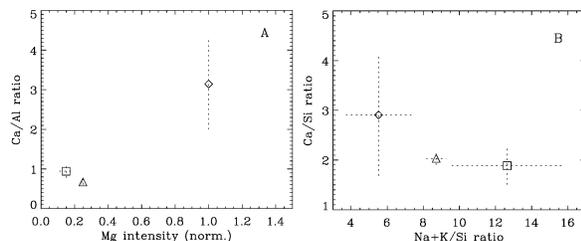


Figure 3: A. Intensity ratio Ca/Al vs Mg intensity; B. Intensity ratios Ca/Si vs (Na+K)/Si for picritic basalt (square), picritic glass (triangle) and DaG 476 (diamond).

The picrites samples are alkali-rich and Mg-poor compared to the shergottite DAG 476 (figure 3). Finally, the meteorite is clearly discriminated for its clinopyroxene-rich composition, as shown by its high Ca/Si and Ca/Al ratios. To interpret LIBS signal in terms of textural variations, Figure 4 presents the Relative Standard Deviation (RSD) obtained on Ca 616.38 nm /Al 308.31 nm intensity ratios, as a function of grain size in the matrix (expressed in μm^2). To encompass wider textural range, we add in the present study the tephrite named "103 G" which presents an aphanitic texture and the basalt named "43G" with coarser grain-size. An obvious positive correlation between grain size from glassy picritic target to coarse grained size can be observed.

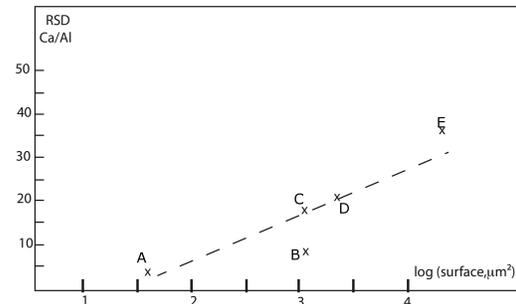


Figure 3 : RSD on Ca/Al for each studied sample versus their crystal size (in μm^2).

Thompson *et al.* [8] distinguished successfully two different SNC meteorites, DaG 476 (picritic shergottite) and Zagami (basaltic shergottite), from their CaO and MgO contents. However, their study was based on calibration curves used to determine their concentrations, that require a large panel of calibration standards. Other studies using LIBS on meteorites were also performed [9,10], using Calibration-free technique [11] to retrieve the chemical composition of these samples, in order to better classify them. These studies are based on the sample compositions, always hard to retrieve by LIBS technique. Our study is more specifically developed for MSL first quick interpretations, thus significant elemental ratios are only required.

Conclusion: Our method presents a quick-look interpretation for the LIBS spectra which can be used initially upon receipt of Curiosity data. The variation calculated on different key elemental ratios such as Ca/Si, Ca/Al or Mg/Si is useful for a rapid approach of the rock description, such as the presence of phenocrysts or the mineral proportions. This study confirms that RSD on definite LIBS ratios can be used for the estimate of the phenocryst size and the rock granularity. ChemCam will probably be largely used for the first determination of the rocks and soils, helping for the further interpretation obtained by the other on-board instruments and helping for the next analyses processing.

References: [1] Wiens *et al.* (2005), *LPSC 36th*, #1580. [2] Maurice *et al.* (2005), *LPSC 36th*, #1735. [3] Maurice S. *et al.* (2009) *LPSC XXXX*, # 1864. [4] McSween H-Y *et al.* (2006) *JGR*, *111*, E02S10. [5] Fabre C. *et al.* (2011) *Spectr. Chim. Acta Part B*, *66*, 80-89. [6] Cousin A. *et al.* (2012) *Spectr. Chim. Acta Part B*, *in press*. [7] Maurice S. *et al.* (2007) *LPSC XXXVIII*, # 1563. [8] Thompson J-R *et al.* (2006) *JGR*, *111*, E10. [9] Dell'Aglio M. *et al.* (2010) *Geoch. and Cosmoch. Acta*, *74*, 7329-7339. [10] De Giacomo A. *et al.* (2007) *Spectr. Chim. Acta Part B*, *62*, 1606-1611. [11] Ciucci A. *et al.* (1999) *Applied Spect.*, *53*, 960-964.