

ROCKS IDENTIFICATION AT THE SURFACE OF MARS BY REMOTE LASER-INDUCED BREAKDOWN SPECTROSCOPY AND CHEMOMETRICS. J.-B. Sirven¹, B. Sallé², P. Mauchien¹, J.-L. Lacour¹, S. Maurice³, G. Manhès⁴, R.C. Wiens⁵, S. Clegg⁵ and the ChemCam team. ¹CEA Saclay, DEN/DPC/SCP (91191 Gif sur Yvette Cedex, France ; patrick.mauchien@cea.fr), ²Noveltis (2 avenue de l'Europe, 31520 Ramonville Saint Agne, France ; beatrice.salle@cea.fr), ³CESR, Observatoire Midi-Pyrénées (9 avenue du Colonel Roche, 31400 Toulouse, France ; sylvestre.maurice@cesr.fr), ⁴IPGP (4 place Jussieu, 75005 Paris, France ; manhes@ipgp.jussieu.fr), ⁵LANL (Los Alamos, NM; rwiens@lanl.gov)

Introduction: Remote Laser-Induced Breakdown Spectroscopy (LIBS) has been selected as part of the ChemCam instrument package for the Mars Science Laboratory (MSL) rover, scheduled to be launched in 2009. ChemCam was selected for MSL largely because the LIBS laser can remotely remove dust layers and perform depth profiles through weathering coatings to reveal unaltered samples. [1,2] The LIBS technique allows both qualitative and quantitative elemental analysis of a wide range of materials. However, as for any method of solid samples analysis, the accuracy of quantitative results is often compromised by the so called matrix effects, which means that the analytical response is influenced by the physical properties of the sample and by its overall chemical composition. Matrix effects were investigated in a previous work as well as the way of compensating them through different normalization methods [3]. In a laboratory, these effects can be partially overcome by applying one calibration curve for each element contained in any substrate of interest. This approach assumes that the sample matrix is known and that reference samples are available for calibration. In other words, the identification of the matrix is required before performing quantitative measurements. In this paper we focus on the identification of rocks by LIBS as a first step of the analysis, enabling the subsequent use of an appropriate calibration curve. This is done with the help of advanced tools for spectral multivariate analysis. Principal Components Analysis (PCA), Soft Independent Modeling of Class Analogy (SIMCA) and Partial Least-Squares Discriminant Analysis (PLS-DA) [4,5] are used to build statistical models which are then able to recognize rocks types from LIBS spectra.

Experiment: The studies were performed on a series of natural rock samples: basalt (ES9206), limestone (RJ3), gabbro (OT9101), trachy-andesite (ES9106), trachyte (ES9101) and obsidian (LMG Little Mountain Glass). Their "reference" elemental compositions, determined by the ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) and ICP-MS (ICP-Mass Spectrometry) techniques, are given with uncertainties in Refs. [6-8]. These samples were analyzed in Martian conditions using the LIBS setup described in Refs. [3,9]. 50 spectra were acquired for each sample at different places on the surface.

Spectra treatment: The three methods which we adopted use entire spectra as input data. PCA compresses the experimental spectra so that the whole dataset (6 rocks*50 spectra*8000 points) be easily observable in a low-dimension space (usually a plane). This enables one to visualize similarities between spectra and to identify classes of samples (i.e. rocks). SIMCA uses PCA for each class of samples and identifies new samples from their membership prob-

ability for each class. PLS-DA calculates a model that predicts the value of a series of dummy variables (as many as the number of classes). These values are then predicted for new spectra in order to allocate them to a class. Calculations were done with the Simca-P 11.5 software (Umetrics).

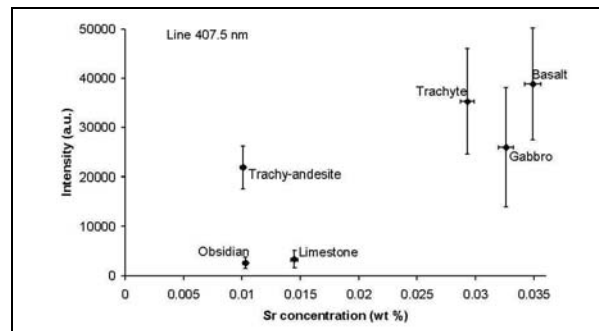


Fig. 1: Multi-matrix calibration curve for Sr.

Results: Fig. 1 shows the intensity of the 407.5 nm Sr line as a function of Sr concentration in each rock. The matrix effect is clearly visible since the points do not align along a line. This well illustrates the difficulty of quantitative analysis when dealing with different rocks types.

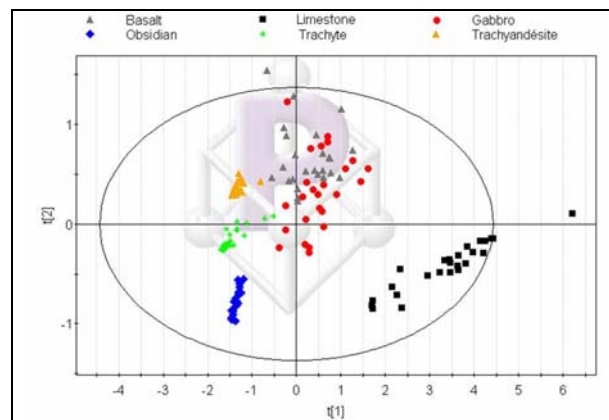


Fig. 2: PCA of spectra from 6 rocks (projection onto the first 2 principal components).

Fig. 2 shows the results of PCA. The axes of the figure represent the coordinates of the spectra along the principal components, i.e. linear combinations of the intensities at the different wavelengths. These combinations are calculated so that they convey the major part of the information contained in the whole dataset. In the case presented on Fig. 2, the first

two principal components represent the quasi-totality, namely 91%, of the global variance. We see that limestone and obsidian are clearly distinguishable, which is logical since the composition of the first one is very different from other rocks and since the second one has different physical properties (it is a natural glass). Trachyte and trachy-andesite spectra also form distinct clusters. Basalt and gabbro have almost exactly the same composition, yet we see that their spectra are partially separated. Moreover, if we ignore the 4 outliers at the top of the graph, gabbro spectra are more dispersed than basalt ones, in accordance with visual observation showing that gabbro is more coarse-grained than basalt. Doing a successive PCA on the spectra of these two rocks enables to better discriminate them and provides a physical interpretation of this result, since the direction that separates the two clusters was shown to be correlated to hydrogen, i.e. this element is discriminant for these samples. This is illustrated on Fig. 3.

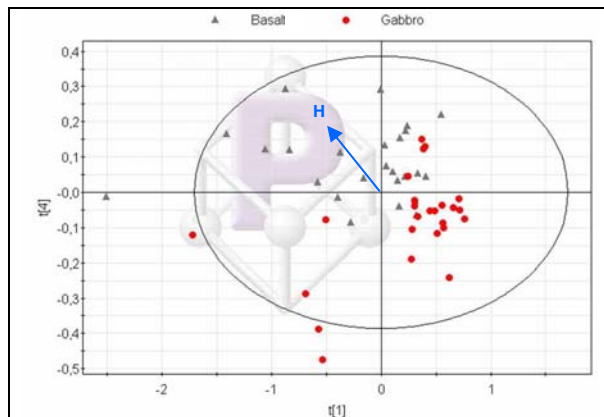


Fig. 3: PCA of basalt and gabbro spectra. The direction of separation between the two rocks is correlated to hydrogen.

SIMCA was tested for binary identification, but led to poorer results than PCA. Clusters of spectra were generally less well defined than in the case of PCA. Fig. 4 shows what we obtained in the best case, i.e. the discrimination between trachyte and trachy-andesite. The figure axes represent the residuals of the projection of each sample onto the PCA model calculated for each class, therefore spectra from each rock should be located on a low-value region for one axis and on a high-value region for the other. Spectra of other rocks should be situated in the upper-right part of the graph, as well as false negatives (i.e. spectra which were not classified as one of the two rocks whereas they should have been), as indicated on Fig. 4.

Finally we used PLS-DA for identifying the sample matrix. Similarly to PCA, a PLS-DA model calculates linear combinations of the spectral intensities in order to predict an arbitrary target value for each class, usually 1 for the class of interest and 0 for the others. For each rock predictions were performed on 10 spectra which were not used for the model calculation. Table 1 shows that our laboratory results are

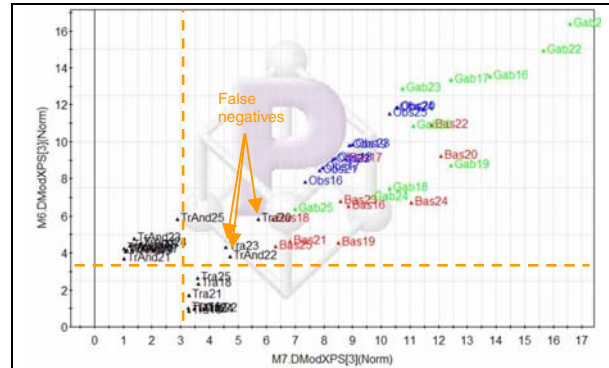


Fig. 4: SIMCA results for the discrimination of trachyte and trachy-andesite.

extremely promising since the rate of correct classification is 100% for 5 rocks out of 6. It is particularly noticeable that the 2 trachy-andesite spectra that were not identified as trachy-andesite were not identified as another rock either, i.e. they are not false positives but were detected as completely unknown, which is a better result.

Rock	Rate of correct classification
Basalt	10/10
Limestone	10/10
Gabbro	10/10
Obsidian	10/10
Trachyte	10/10
Trachy-andesite	8/10

Table 1: PLS-DA results for the identification of rocks.

Conclusion: The feasibility of rocks identification by remote laser-induced breakdown spectroscopy in simulated Martian conditions is investigated. Aside from the intrinsic qualitative result, rocks identification has a great interest as a preliminary step before concentration measurements. Three multivariate spectra treatments (PCA, SIMCA, PLS-DA) are tested to classify the different rocks. PLS-DA yields the best results with an excellent rate of correct classification for each rock. For the ChemCam instrument, comprehensive models have to be built in the laboratory from as many rocks as possible so that the prediction of the identification in the field be the most accurate.

References: [1] Cremers D.A. (1987) *Appl. Spectrosc.* 41, 572-578. [2] Palanco S. et al. (2002) *Spectrochim. Acta Part B* 57, 591-599. [3] Sallé B. et al. (2006) *Spectrochim. Acta Part B* 61, 301-313. [4] Massart D.L. et al. (1988) *Chemometrics : a textbook*, Elsevier Science Publishers B.V. [5] Martens H. et al. (1989) *Multivariate calibration*, John Wiley & Sons. [6] Poitrasson F. et al. (1998) *Bull. Volcanol* 60, 213-223. [7] Poitrasson F. et al. (1995) *J. Petrology* 36, 1251-1274. [8] Cantagrel F. et al. (1994) *Geostand. Newslett.* 18, 123-138. [9] Sallé B. et al. (2006) *Lunar Planet. Sci.* XXXVII 1560.