CHEMCAM LIBS INSTRUMENT : COMPLETE CHARACTERIZATION OF THE ONBOARD CALIBRATION SILICATE TARGETS (MSL ROVER) C. Fabre (G2R, Nancy Université, France, cecile.fabre@g2r.uhp-nancy.fr), S. Maurice (CESR, Toulouse, France), R. Wiens, V. Sautter and the ChemCam team.

Introduction: To be launched in 2011, the ChemCam (Chemistry Camera) instrument suite will provide remote sensing for the Mars Science Laboratory (MSL) rover [1, 2] . The lander will carry body-mounted calibration targets consisting of synthetic silicate glasses, a natural volcanic glass (macusanite), and four sulfate-bearing ceramics [3]. The certification of the homogeneity of the different synthetic silicate glasses and the macusanite at the scale of laser spot sampling are necessary to validate their selection.

Basaltic calibration targets: the compositions of theses silicate targets have been chosen to simulate the expected rocks on the Mars surface. The typical compositions are those observed for Picritic, Basaltic shergottite and Norite basalts [4]. These synthetic glasses were prepared from carbonate, oxide or sulfur powders and a natural obsidian glass known as Macusani has been added to this set. Trace elements of Ba, Sr, Cr, or Li, from hundreds to thousands of ppm, have been included to replicate alteration products on Mars surface. Before the launching of the MSL rover, a first set of ChemCam calibration targets has been done in order to test them mechanically, before the decision to proceed on the realization of the definitive targets. Shock test (2000g and 4000g shock exploratory test) and temperature cycle tests have been successful passed.

Chemical analysis: As these silicate glasses will be used as calibration targets for the in situ LIBS analyses, their composition were carefully controlled at different scales using Electronic microprobe and Femto-Laser Ablation ICP MS. Two separate sets of chemical analyses were undertaken : Analysis of 12 elements using Microprobe electronique technique [4], and 38 elements using femto LA ICP-MS technique (Observatoire Midi Pyrénées, University Toulouse III) included trace and rare earth elements (Table 1). Concentrations of major, REE and trace elements were determined in situ at the LIBS ablation spot size around 200 µm lateral resolution. Access to REE is important for the detailed characterization of natural glass macusani that is poorly described in the litterature.

Femto LA ICP-MS analysis: Eighteen elemental analyses in femto LA ICP MS were completed for Norite, Shergottite and Picrite samples, and twenty five elements were detected for the natural glass Macusani. Measured spot laser ablation is around 50 µm of diameter which replicates the smallest laser spot size for in situ LIBS analysis. Two distinct zones were tested for each sample. Mean concentrations from trace elements to major elements for macusani sample are reported in Table 1. All of the samples, natural or synthetic present a very good homogeneity with a RSD lower than 10% for concentration higher than 0,01 oxide weight % (Figure 1). Comparing to the previous analysis obtained in electronic microprobe [4], a very good agreement in the concentrations can be noticed between the two sets of analysis (Figure 2).

Macusani glass analyis: The natural target presents, as expected from the few literature available, high content in Li (3500 ppm), B (1570 ppm), K (3,4 %), and rather high level in Mn (500 ppm) and Cs (570 ppm) comparing to the values obtained using femto-LA-ICP-MS for the three other samples. As calibration curves should be established for semi to quantitative analysis, its low concentration in Ti, Sr and Ba (at ppm level) will be a fine aid for the check of emission peak locations on the LIBS spectra. REE and ultra trace amounts are generally under 3 ppm, up to 18 ppm for Ta and U.

As few descriptions are available on these specific natural samples, specific Scanning Electron Microscope observations have been carefully undertaken to control the possible presence of natural minerals: Monazites, Zircons and alumni-silicate needles (Figure 3) that do not exceed twenty micrometers long. Monazites are enriched in Phosphorus and Cerium, around 50 wt % and 35 wt% respectively explaining the rather high contents in P up to 2000 ppm. SEM analyses on various monazites and zircons, testify that their compositions are quite constant mineral to mineral. For the Al/Si mineral, they are probably Andalusite minerals Al_2SiO_5, already reported by Virgin et al. (1969).

Conclusion : Regarding to the LIBS diameter ablation, zircons and monazites will not affect the calibration, and we can conclude that this volcanic glass presents a very good homogeneity at this scale. RSD obtained for femto LA ICP-MS and electronic microprobe analyses generally lower than 15% for major to low elements, are those required for such analytical standard.

Table 1: Concentrations of major, trace and rare earth elements obtained using Femto LA ICP MS analysis on the obsidian glass, macusani target.

	composi-tion	RSD %		composi-tion	RSD %
Li7	3528,4	6,0	Zr90	13,5	12,4
Be9	35,6	6,5	Nb93	55,2	14,7
B11	1572,7	5,6	Mo95	0,6	
Na23	*29367,1*	*5,9*	Cs133	568,6	6,5
Mg25	*97,7*	*3,8*	Ba137	1,3	27,7
Si28	*346782,3*	*4,4*	La139	3,16	144,1
P31	2016,5	5,3	Ce140	6,52	142,3
K39	*34152,4*	5,6	Nd146	2,04	109,6
Ca44	1904,7	25,0	Sm147	2,16	100,9
Sc45	10,8	41,5	Eu153	0,21	67,7
Ti47	251,6	7,6	Gd157	1,39	94,3
Cr52	2,8	50,9	Dy163	1,03	52,8
Mn55	499,7	9,3	Er166	0,32	39,3
Fe56	4175,7	11,0	Yb172	0,36	36,8
Fe57	3975,7	15,0	Lu175	0,07	61,3
Cu63	2,4	15,6	Ta181	18,3	10,0
Zn66	108,6	7,4	Pb208	9,4	21,3
Sr88	1,3	19,9	Th232	2,5	141,7
			U238	17,3	10,3

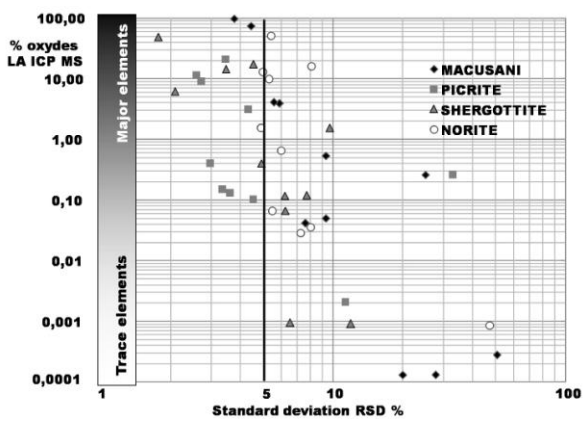

Figure 1: Femto LA ICP MS analysis and their Relative Standard Deviation obtained for the four synthetic silicate targets.

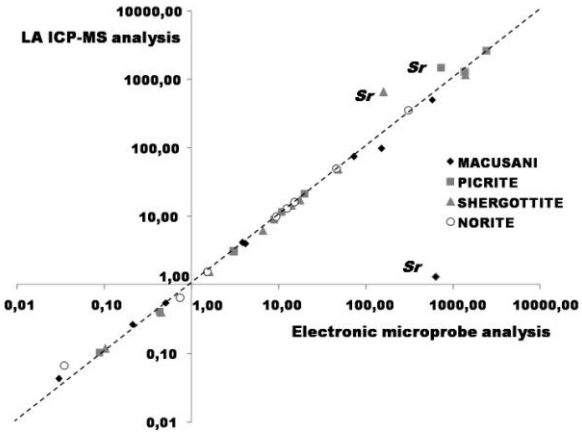

Figure 2 : Comparison between the two sets of analyses using electron microprobe and LA ICP MS in situ analysis.

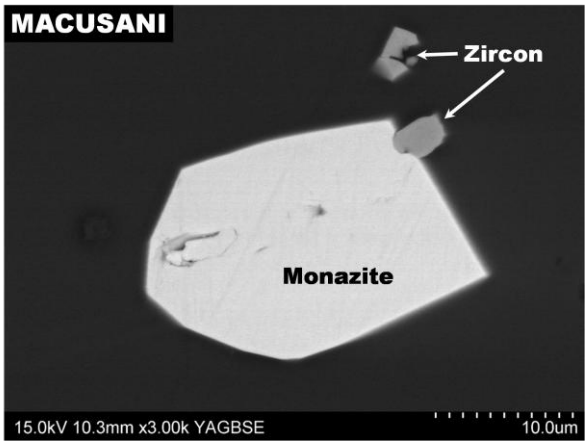

Figure 3 : Back Scattering Electronic Microscopy of minute Zircon and Monazite minerals, observed in the macusani glass sample.

References:

[1] Wiens et al. (2002), *JGR, 107* . [2] Wiens et al. (2009) *LPS XXXX*, abstract # 1461. [3] Vaniman et al. (2009) *LPS XXXX*, abstract # 2269. [4] Fabre et al. 2009 *LPS XXXX*, abstract # 1502.