Characterization of the SuperCam LIBS Calibration Targets. A. Cousin[1], S. Maurice[1], F. Rull[2], C. Fabre[3], V. Sautter[4], G. Montagnac[5], P. Beck[6], C. Drouet[7], J.M. Madariaga[8], J. Aramendia[8], L. Gomez-Nubla[8], J. Manrique[2], P.-Y. Meslin[1], P. de Parseval[9], S. Gouy[9], G. Chevallier[7], G. Dromart[5], S. Bernard[4], R. Wiens[10], O. Gasnault[1], O. Forni[1], J. Lasue[1], J. Moros[11], J. Laserna[11]. [1]IRAP, Toulouse, France (agnes.cousin@irap.omp.eu), [2]University of Valladolid, Spain, [3]Université de Loraine, France, [4]IMPMC, Paris, France, [5]ENS de Lyon, France, [6]Université Grenobles Alpes, France, [7]CIRIMAT, Toulouse, France, [8]University of the Basque Country (UPV/EHU), Spain, [9]Centre Raimond Castaing, Toulouse, France, [10]LANL, Los Alamos, USA, [11]University of Malaga, Spain.

Introduction: Mars2020 is the next NASA mission to Mars. This mission presents four science objectives: 1/ Study of Mars past habitability (in continuity to Curiosity's work), by identifying past environments that could have been favorable for supporting microbial life, 2/ Search for signs of past microbial life in rocks observed in such environments, 3/ Collect and Cache samples; these core rocks and soil samples will then be stored on the martian surface and 4/ Prepare for future Human missions, by testing the oxygen production from the martian atmosphere.

The SuperCam instrument has been selected to be part of the payload. This instrument is the next generation of ChemCam [1,2]: it consists of a Laser Induced Breakdown Spectroscopy (LIBS) technique in order to assess the chemical composition of the samples, but this time this capability is also coupled with Raman and IR spectroscopies in order to have access to the mineralogical compositions. SuperCam consists also of a color micro imager and a microphone. After cleaning the dust with the first LIBS shots and thanks to its remote sensing techniques, this instrument will thus provide rapid, synergetic, fine-scale (<0.5 mm) mineralogy and chemistry of samples as well as color imaging.

Due to different parameters on LIBS, Raman and IR spectroscopies as well as for the imager, in situ calibrations with known targets is of prime importance. To this purpose the rover will cary a set of 31 calibration targets for the SuperCam instrument [3]. Five targets are dedicated to the imager, two to the IR technique, two for the raman, and twenty two for the LIBS technique.

These LIBS targets need to be particularly homogeneous at fine scale due to the small footprint of the technique, around 300 microns. Thus, each target (set of 6 replicates) has been characterized by multiple techniques: continuous Raman, XRF, LIBS and EMPA (Electron MicroProbe Analysis). This study will present a subset of the results obtained from the electron microprobe analyses (quantitative information), and from the LIBS analyses (qualitative information), as well as their correlations.

LIBS Calibration Targets: For the LIBS technique, which gives access to the chemical composition of the sample, the need is to cover a wide range of compositions, as well as a wide range of rock types in order to account for chemical matrix effects. Also, minor and trace elements should be present in different amounts in order to produce in situ calibration curves. A total of 22 LIBS calibration targets have been developed. One of them corresponds to the shergottite-like target that was already onboard Curiosity [4], and will serve for cross-calibration between SuperCam and ChemCam. One target is dedicated to the wavelength calibration of the LIBS technique and corresponds to a Ti-plate, the same as the one used for ChemCam.

Stoichiometric targets. From the ChemCam experience, targets with stoichiometric compositions are of great interest to calibrate key elemental ratios such as Al/Si, (Fe+Mg)/Si, Na+K/Si, Ca+Na/Si, Na/K which are commonly used for terrestrial and martian geochemical comparison. Natural minerals such as feldspars, pyroxenes and olivines that are widespread on Mars are thus good targets for this objective. We have selected six compositions: feldspars will be represented by an orthose and an andesine; one olivine with a Fo#70; and pyroxenes with a diopside, ferrosilite and enstatite. All these targets come from natural minerals that have been crushed to <60 microns and then flash sintered.

Trace-elements enriched targets. Five targets dedicated to trace and minor elements have been investigated. They all have a trachy-andesitic composition, doped with elements of interest: Sr, Rb, Ba, Cr, Cu, Li, Ni, Zn and Mn. Each target contains these elements at a different content (lowest/highest value constrained from ChemCam experience at Gale) in order to provide a calibration curve for each trace/minor element. These targets have been synthesized from powder mixtures and then melted in order to make a glass. This glassy material was then crushed in order to proceed to the flash sintering.

Standard targets. Eight targets will provide a wide variety of rock types, including basalts, sulfates, carbonates. All these targets correspond to well known standards and most of them have been used for the Earth database of ChemCam [5]. Powders from the standards have directly been sintered.

Fluoro-chloro-hydroxy-apatite target. Apatites in martian meteorites are mainly enriched in Cl and H, while F-rich apatites have been observed at Gale crater [6,7]. One apatite composition has been chosen to give a reference for P, Cl, F and H abundances, which are important in order to estimate the halogen budget of the martian mantle. P and H are also relevant for organic detections.

Characterization: Continuous Raman and XRF analyses have been performed in Spain at the University of the Basque Country [8] with the purpose to certificate the homogeneity distribution of compounds and elements in the surface of the calibration targets.

LIBS analyses have been performed in Toulouse at IRAP using the ChemCam replicate, which is close to the SuperCam LIBS instrument. Targets were placed on a martian chamber (P = 6 mbar, with martian-like atmosphere) and the instrument is operated at -10 degrees C. We have performed a grid of 9 random points on all the replicates except the flight and spare models. Each point corresponds to 30 shots. Other LIBS analyses have been performed in Malaga to focus on depth profiles and quantification.

The EMPA have been performed in Toulouse at the micro-characterization center of "Raimond Castaing", with a Cameca SXFive model. We have analysed all the 6 replicates in order to make sure each pellet is homogeneous, but also that they have the same composition. As the LIBS spotsize is around 250 microns, microprobe analyses were done over 3 random squares of 100x100 microns with a 2 microns analysis spotsize. 9 point analyses were performed in each square, and then 10 to 15 selected points have been also performed depending on the number of mineralogical phases in the sample in order to make sure to sample all of them. This gives a worst case scenario for the homogeneity compared to data from the LIBS analyses.

Results: *LIBS analyses*. We have fitted neutral and first-order ionized elemental lines of the most important elements, according to the lines already used for ChemCam univariate calibration [4]. Table 1 shows the standard deviation and the RSD (Relative Standard Deviation) of the BHVO-2 [9] target as an example, calculated from the peak areas. This target, as all other targets, is homogeneous at LIBS scale, with low RSDs (<10 %) for all major elements and most minor elements.

EMPA analyses. All the 6 replicates have been analysed for each standard to look at the homogeneity of each individual pellet, but also to check the consistency between the replicates. Table 2 presents the results obtained for the BHVO-2 target as well as the Andesine target. The Andesine composition is very homogeneous: RSDs are < 10 % when looking at the results obtained on all the 6 pellets, but also for the flight model itself. The BHVO-2 target shows more heterogeneities, with RSD > 15 % even for major elements. This can be explained by the fact that microprobe spotsize is significantly lower than the LIBS spotsize and still lower than the grain size (~50 microns) of the samples.

Besides this scale effect, univariate regression between LIBS and EMPA analyses are satisfying. Figure 1 is an example obtained for the trace element targets concerning the Ba emission line (455.5nm) from LIBS signal versus the BaO content (wt %) from the microprobe. The correlation is very good with a R^2 at 0.97.

Conclusions: SuperCam calibration targets have undergone a complete set of characterization, with microscopic inspection, XRF, Raman, LIBS and microprobe analyses. Even though EMPA analyses reveal some heterogeneous targets at this scale such as BHVO-2, results are encouraging as all the targets are homogeneous at LIBS scale. Also, these results show a good agreement between the EMPA quantitative data and the LIBS signal, which is the main purpose of these calibration targets. These targets are ready for cross-calibrations between the different instruments onboard Mars2020.

BHVO-2	Major elements					
	Al_394nm	Si_288nm	Si_634nm	Ca_318nm	Ca_393nm	Ca_422nm
Stand. Dev.	2.71E-04	3.80E-05	3.91E-04	1.38E-04	5.16E-05	6.09E-05
RSD	2.9	4.6	3.7	7.7	7.0	3.7
	Fe_438nm	Fe_404nm	Fe_260nm	Mg_285nm	Mg_448nm	
Stand. Dev.	1.78E-05	1.66E-05	3.29E-05	5.15E-05	6.76E-05	
RSD	4.7	4.7	3.3	7.0	7.0	
	Minors elements					
	Na_589nm	Na_818nm	K_766nm	Ti_335nm	*Cr_327nm*	*Mn_404nm*
Stand. Dev.	1.35E-03	5.38E-05	1.75E-04	6.19E-05	*7.26E-06*	*1.42E-05*
RSD	4.6	8.0	7.3	5.9	*33.7*	*25.4*

Table 1: LIBS Standard Deviation and RSD (%) obtained on the BHVO-2 target (from 4 replicates), for major and minor elements. Only few lines are shown for clarity.

BHVO-2 all replicates											
	Na2O	**Al2O3**	**SiO2**	**CaO**	K2O	MnO	**FeO**	**MgO**	TiO2	Cr2O3	Total
Average	2.37	**12.91**	**51.89**	**10.81**	0.74	0.18	**11.62**	**6.49**	2.98	0.03	100.02
Stand. Dev.	1.83	**9.45**	**11.61**	**5.5**	1.02	0.14	**12.24**	**7.85**	5.25	0.06	0.77
RSD	77.56	**73.14**	**22.36**	**50.87**	137.3	77.53	**105.34**	**120.99**	176.11	185.97	0.77
BHVO-2 flight model											
	Na2O	**Al2O3**	**SiO2**	**CaO**	K2O	MnO	**FeO**	**MgO**	TiO2	Cr2O3	Total
Average	1.98	**9.39**	**55.08**	**12.32**	0.85	0.21	**10.37**	**7.58**	1.79	0.01	99.58
Stand. Dev.	1.82	**6.61**	**8.55**	**5.82**	1.21	0.12	**5**	**6.22**	0.82	0.01	0.47
RSD	91.72	**70.47**	**15.52**	**47.22**	142.84	56.36	**48.23**	**82.12**	45.76	76.37	0.47
Andesine - all replicates											
	Na2O	**Al2O3**	**SiO2**	**CaO**	K2O	MnO	FeO	MgO	TiO2	Cr2O3	Total
Average	**6.62**	**25**	**59.13**	**8.2**	0.43	0.04	0.49	0.42	0.02	0.04	100.39
Stand. Dev.	**0.43**	**1.31**	**1.26**	**0.73**	0.24	0.04	0.42	0.35	0.03	0.05	0.76
RSD	**6.56**	**5.25**	**2.12**	**8.95**	55.93	87.93	85.45	83.56	172.5	140.99	0.76
Andesine - flight model											
	Na2O	**Al2O3**	**SiO2**	**CaO**	K2O	MnO	FeO	MgO	TiO2	Cr2O3	Total
Average	**6.68**	**24.87**	**59.13**	**8.08**	0.44	0.04	0.58	0.48	0.01	0.06	100.37
Stand. Dev.	**0.44**	**1.16**	**1.05**	**0.65**	0.29	0.04	0.52	0.49	0.02	0.1	0.79
RSD	**6.6**	**4.67**	**1.77**	**8.04**	64.76	85.47	90.11	102.77	155.36	180.59	0.79

Table 2: Average composition, Standard Deviation and RSD (in %) from the microprobe analyses on the BHVO-2 and Andesine targets. Results are shown for each target first from all the 6 replicates, and then for the flight model only. Major elements are in bold.

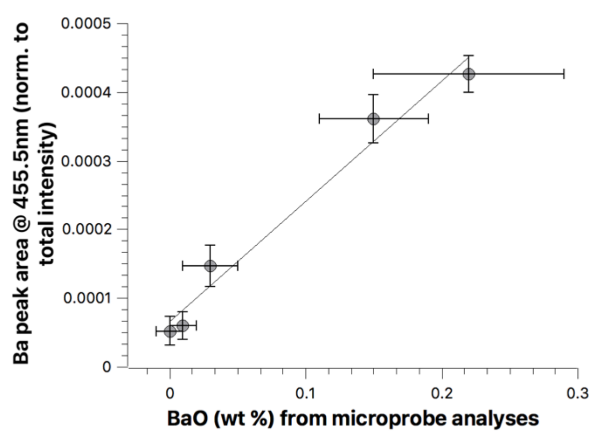

Figure 1: Ba signal @ 455.5 nm from LIBS analyses versus BaO content from microprobe data. Error bars correspond to the standard deviation. For LIBS, it is obtained from the all the points acquired from the 4 replicates, and from all the 6 replicates analysed by microprobe.

References: [1]Wiens et al., SSR, 2012; [2]Maurice et al., SSR, 2012; [3]Cousin et al., LSPC 48 #2082, 2017; [4]Fabre et al., Spect. Chem. Acta B., 2011; [5]Clegg et al., Spect. Chem. Acta B., 2017; [6] Meslin et al., LPSC 47 #1903, 2016; [7]Forni et al., LPSC 48 #1838, 2017; [8]Aramendia et al., TrAC-Trend Anal. Chem., 2018; [9] Wilson et al., USGS, 1997.