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SuperCam calibration targets on board the perseverance rover: Fabrication and quantitative characterization

Agnès Cousin, Violaine Sautter, Cécile Fabre, Gilles Dromart, Gilles Montagnac, Christophe Drouet, Pierre-Yves Meslin, Olivier Gasnault, Olivier Beyssac, Sylvain Bernard, et al.

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SuperCam Calibration Targets on Board the Perseverance Rover: Fabrication and Quantitative Characterization

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R.C. Wiens

Abstract

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The Perseverance rover is exploring Jezero crater on Mars since February 2021. SuperCam instrument is part of the scientific payload, combining five different techniques in order to characterize the targets to sample: LIBS (Laser-Induced Breakdown Spectroscopy), Raman and Visible and Infrared (VISIR) spectroscopies, Sound Recording and a colored Imager. Thirty-six calibration targets have been developed for this instrument. Twenty-three of these calibration targets are dedicated to the LIBS technique, corresponding to rocks and/or minerals. Their mineralogical signature is also of interest with Raman and VISIR techniques. The choice and the fabrication of these calibration targets have been made in order to fulfill the science intents of the mission, but also the technical and science intents of each of the SuperCam technique. These calibration targets have been spectrally characterized and they have shown to be chemically homogeneous at the SuperCam LIBS scale. Their elementary compositions are given, using two different quantitative

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methods. The composition of the calibration targets will be used as reference for future assessment of the quantitative capability of the SuperCam LIBS technique.

Keywords: Mars, SuperCam, Mars2020, Perseverance, LIBS

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1. Introduction

The Mars2020 *Perseverance* rover was launched on July 30th, 2020, and landed at Jezero crater on February 18, 2021. This mission is contributing to the four long-term science goals of NASA’s Mars Exploration Program. In short form, these goals consist of [1]: 1)Search for habitability, 2)Characterize climate evolution, 3)Characterize the geology of Mars, and 4)Prepare for human exploration. The prime objective of this mission is the search for signs of past microbial life on Mars, specifically:

- 9 1. Look for habitability, *by identifying if past conditions were capable of*
10 *supporting microbial life*
- 11 2. Seek biosignatures, *by searching for any signs of past microbial life in*
12 *such an environment*
- 13 3. Cache samples, *by selecting, drilling and collecting rocks and soils of*
14 *interest*
- 15 4. Prepare for human explorations, *by testing production of oxygen from*
16 *the CO₂-rich martian atmosphere*

17 On-board the *Perseverance* rover, the SuperCam instrument [2, 3] is be-
18 ing used as a remote-sensing facility to analyze rocks and soils that are up
19 to 7 m from the rover (and up to infinity for the imager and visible/near-
20 infrared (VISIR) techniques). This instrument has heritage from the suc-
21 cessful ChemCam instrument [4, 5] on-board the Curiosity rover of the Mars
22 Science Laboratory (MSL) mission, which landed in 2012 in Gale crater.
23 SuperCam is the first instrument to examine both the elementary and min-
24 eralogical analysis of a target on Mars. It does so by using a suite of five
25 coaligned techniques : just like ChemCam, it uses the Laser Induced Break-
26 down Spectroscopy (LIBS) technique to determine the elemental composition
27 of the targets, but it also uses Raman (for the first time in planetary science)
28 and VISIR (for the first time *in situ* near-infrared spectroscopy in the 1.3-2.6
29 μm range) spectroscopic methods in order to access some mineralogical and
30 structural information. A microphone provides a mean to study the physical
31 parameters of the sampled rocks (such as hardness [6]) as well as to some
32 atmospheric parameters (wind direction [7]). The context for these chemi-
33 cal and mineralogical analyses is provided by a color Remote Micro-Imager.

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34 More details about each technique can be found in [2, 3, 8]. The SuperCam
35 sampling footprint varies between 0.3 mm for LIBS at close range (1.56 m,
36 distance of the calibration targets) to 1 cm for IR at 7 m distance, and larger
37 at longer distances.

38 In order to monitor the instrument’s health over time as well as to assess
39 the quality of the data, there is an on-board suite of SuperCam Calibration
40 Targets (SCCT). Thanks to the ChemCam experience, SuperCam’s LIBS
41 targets are more comprehensive and better prepared than ChemCam’s, and
42 additional targets address each of the new techniques. They are located at
43 1.56 m from the instrument entrance window. The SCCT sample holder is
44 significantly larger than that on ChemCam. An overview of the mechanical
45 aspects and environmental testing of the targets is given in [9]. These SCCTs
46 have been selected and prepared in accordance with the landing-site miner-
47 alogies observed from orbital data, in order to address the several science
48 intents of the mission.

49
50 This paper focuses on the LIBS (also called ”geological”) SuperCam Cal-
51 ibration Targets. Considering our experience with the ChemCam instrument
52 and the major importance of the calibration for quantitative LIBS charac-
53 terization, most of these targets are dedicated to this technique, even though
54 some of them will be used as well for the Raman and VISIR spectroscopy
55 techniques. We first describe the selection of each type of targets, depend-
56 ing on the different objectives. The fabrication process, which is relatively
57 new [10], is also explained in detail. Then, a summary of all the qualita-
58 tive characterizations is presented, along with an overview of the SCCTs’

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9 59 spectral signature as seen by all of the SuperCam techniques. The main
10 part of the paper focuses on the quantitative analyses of these targets with
11 60 part of the paper focuses on the quantitative analyses of these targets with
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13 61 third-part techniques as Laser Ablation coupled with a Inductively Coupled
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15 62 Plasma Mass Spectrometry (LA-ICP-MS) and Electron Micro Probe Anal-
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17 63 yser (EMPA). They are well known for their accuracy and precision, and
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19 64 are fundamental to determine the reference composition of these calibration
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21 65 targets. Finally, the use of the SCCTs on Mars is presented.
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23 66

26 67 **2. Overview of the SuperCam Calibration Targets**

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29 68 The on-board calibration targets were designed and implemented to achieve
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31 69 several technical and science objectives related to each technique (Imager,
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33 70 VISIR, Raman, LIBS, microphone). Even though SuperCam has been exten-
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35 71 sively tested and calibrated before launch, it is important to continue those
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37 72 calibration activities on Mars. The overarching objectives of the on-board
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39 73 calibration targets are the following:

- 40
41 74 1. To perform a health check and performance status after launch, cruise,
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43 75 entry-descent-landing, and mast deployment;
- 44
45 76 2. To evaluate the actual performance in a real operational environment,
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47 77 first and foremost the effects of temperature, pressure, and dust;
- 48
49 78 3. To track any performance drift with time due to component aging and
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51 79 dust accumulation;
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53 80 4. To provide a “ground truth” solution for SuperCam LIBS quantitative
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55 81 models.

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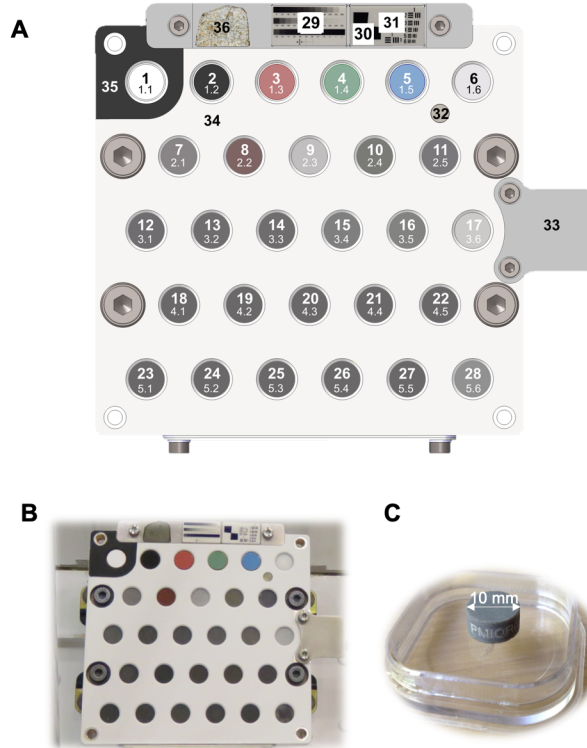


Figure 1: SuperCam Calibration targets on their sample holder. A: Sketch with position number and target number; B: Picture of the Flight Model, mounted on the Rover at JPL. C: Picture of the PMIOR0507 target (Orthoclase, target number 12) before being mounted.

82 The number of targets was constrained by the total mass budget allocated
83 to the SuperCam calibration target set [9]. A total of 36 targets were selected,
84 as shown in Figure 1. In this section, we review the overall objectives of the
85 calibration targets for each technique, with a particular focus on the LIBS
86 targets.

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87 *2.1. Remote Micro Imager dedicated targets*

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11 Evaluation of the SuperCam Remote Micro Imager (RMI) makes use of
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13 89 five specific targets. Two geometric plates are dedicated to 1) diagnosing the
14
15 90 resolution and the modulation transfer function (MTF: target 29 in Figure
16
17 91 1 ; 2) characterize dynamic performance and point spread function (PSF)
18
19 92 (targets 30 and 31 in Figure 1). There are also three colored targets for the
20
21 93 color balance and for analysis of hot pixels (targets 3: Red, 4: Green and 5:
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23 94 Cyan - Figure 1). More details about these targets can be found in [9], and
24
25 95 about the RMI implementation and performance in [2].
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29 97 Another particular target, a slice of a martian meteorite (ref. North West
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31 98 Africa, NWA 10170, target 36 - Figure 1), is of interest for the imager. This
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33 99 meteorite is classified as an olivine-phyric shergottite, as it contains olivine
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35 100 phenocrysts [11, 12]. In fact, this meteorite was carried into space by the
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37 101 French astronaut T. Pesquet to the International Space Station (ISS) from
38
39 102 November 2016 to June 2017. Following its return to Earth, a slice was in-
40
41 103 corporated into the SCCT holder, close to the two RMI geometric plates.
42
43 104 This target is a tribute to the sample return that the Mars2020 mission is
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45 105 preparing. More details about the story of this meteorite can be found in [2].
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49 107 *2.2. VISIR dedicated targets*

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51 108 The VISIR (Visible and Infra-Red) targets are used for radiometric cal-
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53 109 ibrations. There are two main standards: a white target (target 1 - Figure
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55 110 1) used for the white balancing of images, and to obtain relative reflectance
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57 111 spectra by ratioing two successive spectra of the sun-lit white target and the
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10 112 scientific target; and a black target (target 2 - Figure 1) used for VISIR bore-
11 113 sight registration. More details can be found in [9] and [13, 8]. In particular,
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13 114 the laboratory characterization of the VISIR-dedicated SCCT presented in
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15 115 Section 5.2 was designed to match the spectral range and resolution of the
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17 116 body unit and mast unit spectrometers.
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20 21 118 *2.3. Raman dedicated targets*

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23 119 Remote time-resolved Raman spectroscopy is expected to yield informa-
24 120 tion on the mineralogy and crystalline structure of the targeted rocks. The
25
26 121 technical and scientific objectives of the Raman calibration targets are: 1)
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28 122 monitoring the health of the instrument, 2) monitoring the intensity of Ra-
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30 123 man signal of some reference mineral on-board in a true martian environmen-
31
32 124 tal context, 3) testing the detection of organic compounds once on Mars, 4)
33
34 125 documenting the impact of UV radiation on the spectroscopic properties of
35
36 126 organic compounds on Mars surface. To achieve these objectives, Supercam
37
38 127 features two Raman-dedicated targets: a diamond and an organic sample
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40 128 (targets 32 and 6, respectively in Figure 1).

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42 129 The diamond displays a sharp and intense band at 1332 cm^{-1} , and is
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44 130 used for three main purposes: to verify the wavelength calibration with the
45
46 131 band position, to check the alignment between the incident laser beam and
47
48 132 the telescope field of view by checking the band intensity, and to monitor the
49
50 133 instrument's spectral resolution by checking the FWHM of the 1332 cm^{-1}
51
52 134 band .

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54 135 The organic sample is a polyethylene terephthalate (PET, $\text{C}_{10}\text{H}_8\text{O}_4)_n$)
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56 136 exhibiting a strong Raman signature including aromatic, aliphatic and es-

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10 137 ter/carboxylic functional groups. Such molecular groups are expected to be
11 138 found in organic compounds trapped in ancient rocks, and therefore could
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13 139 be searched by SuperCam. Its main objective is to evaluate the capacity of
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15 140 SuperCam to detect organics at the surface of Mars. The ertalyte target can
16
17 141 also be used to check the time-synchronization of the instrument by doing
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19 142 time-sweep experiments: the laser pulse is scanned through time and the
20
21 143 intensity of the Raman signal is plotted against the moment the ICCD gate
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23 144 opens. Another objective is to perform aging experiments by monitoring the
24
25 145 possible degradation of the target under UV radiation. This material was also
26
27 146 selected as the calibration target of the Raman Laser Spectrometer (RLS)
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29 147 onboard the ExoMars Rover [14], and will therefore also be used to compare
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31 148 SuperCam to RLS performance. In addition to these two Raman-dedicated
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33 149 targets, the sample holder paint (target 34) constitutes a third opportunis-
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35 150 tic target, especially interesting as it shows some spectral signatures below
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37 151 1000 cm^{-1} , a spectral range not covered by the two other targets but of high
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39 152 interest for mineralogy.

40 153 Some of the targets devoted to the LIBS technique (next section) are also
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42 154 used for the Raman technique as reference minerals (see part 5.3).

43 44 45 155 *2.4. LIBS targets*

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47 156 The LIBS calibration targets, which are the most numerous, have several
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49 157 instrumental and science objectives. In terms of instrument diagnostics, five
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51 158 main objectives are highlighted in this manuscript: 1) The calibration tar-
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53 159 gets are used to monitor any performance change by frequently analysing the
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55 160 targets using the same instrument parameters. 2) The LIBS technique is sen-
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57 161 sitive to the atmospheric pressure and composition, so on-board calibration

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10 162 targets are important to compare the spectra obtained on Mars with those
11 163 acquired on Earth by mimicking Mars conditions. 3) These calibration tar-
12 164 gets are also useful to better understand the data acquired on Mars targets
13 165 (rocks and soils), as several parameters inherent to the LIBS technique need
14 166 to be investigated on Mars (laser energy, focus, gain). 4) The targets rep-
15 167 resent a subset of the terrestrial database and are being used to correct any
16 168 difference between martian and terrestrial spectra on identical targets; this is
17 169 of great importance to understand the differences between the lab data and
18 170 the Mars data (and avoid potential biases), and to validate the quantification
19 171 models that are being developed for chemical composition [15, 16]; 5) One
20 172 target, the Ti-plate, is mainly dedicated to the wavelength calibration, as on
21 173 ChemCam. The terrestrial database corresponds to more than 330 samples
22 174 that have been analysed with SuperCam setup [comprising an Engineering
23 175 and Qualification Model (EQM) for the Mast Unit coupled with the Flight
24 176 Model (FM) for the Body Unit] at the LANL laboratory (Los Alamos, NM),
25 177 under a Mars-like atmosphere during the calibration campaign of SuperCam
26 178 [3, 2].

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41 179 SuperCam contributes to all of the Mars2020 science objectives: investi-
42 180 gating the geology and geochemistry, studying past environments, and seek-
43 181 ing signs of biosignatures at Jezero crater. Therefore the on-board SuperCam
44 182 calibration targets help fulfill these objectives. Here we point out the scien-
45 183 tific purposes of the LIBS calibration targets. 1) Geology: selected calibra-
46 184 tion targets represent a wide range of rock compositions (silicate-, carbonate-,
47 185 sulfate-, phosphate-bearing), including a subset of igneous minerals, that are
48 186 consistent with the geological expectations at Jezero, and are also consistent

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10 187 with observations at previous landing sites; 2) Geochemical processes: mi-
11 188 nor elements are powerful probes to better constrain geochemical processes
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13 189 that rocks may have undergone. Therefore, the LIBS targets, both natural
14
15 190 and synthetic, have been selected to cover a wide range in minor and trace
16
17 191 element proportions, to assess the limits of detection (LOD) on Mars and
18
19 192 to anchor the abundance calibration curves; 3) Past environments and cli-
20
21 193 mate change: some targets correspond to carbonate, hydrated silicate and
22
23 194 alteration products, some others are enriched in sulfate; 4) Astrobiology: the
24
25 195 LIBS technique is sensitive to the CHNOPS elements, which are important
26
27 196 for life, and therefore several targets contain these elements, along with Cl.
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29 197 Also, high Mn concentrations were identified on Mars at Gale crater with
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31 198 Curiosity [17, 18]; this elements is of great importance to probe oxidizing
32
33 199 conditions at the time of their formation. Si-rich targets are also important
34
35 200 to account for the astrobiological aspect of amorphous silica, which has been
36
37 201 observed already at several landing sites [19, 20, 21, 22, 23, 24, 25, 26];

38 39 202 *2.5. Lessons learned from ChemCam*

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41 203 ChemCam on-board *Curiosity* was the first instrument to use the LIBS
42
43 204 technique to measure the elemental compositions of Mars samples. To mon-
44
45 205 itor the quality of the LIBS spectra acquired during the mission, calibration
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47 206 targets were mounted on board the Curiosity rover. Their LIBS spectra
48
49 207 are regularly compared with spectra obtained in the laboratory of the same
50
51 208 targets and in similar environmental conditions. The ChemCam calibration
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53 209 targets also fulfill two additional objectives. First, they are used to create
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55 210 partial calibration curves that are compared with models developed from the
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57 211 Earth database, as a check on the Earth-based quantitative models; Second,

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212 they are used to check any change in the instrument’s performance, by re-
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11 peating the measurements on the same target over the course of the mission.
12

13
214 There are ten ChemCam calibration targets, each 2 cm wide. They cor-
14
15 respond to samples whose compositions are supposed to mimic that of rocks
16
17 expected on Mars from orbital and previous *in situ* missions, whether mag-
18
19 matic [27] or sedimentary [28, 29]. Three are synthetic glass targets with
20
21 basaltic compositions ranging from picritic, noritic, shergottitic and with
22
23 variable abundances of trace elements; one is a felsic (alkali, aluminum and
24
25 silicon-rich, iron and magnesium-poor) natural magmatic glass that is a ma-
26
27 cusanite from Peru [27]; and four are sulfate-bearing ceramic targets from
28
29 low to high sulfur contents to mimic Martian sediments [28, 29]. One other
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223 target is a graphite, chosen for carbon peak detections, and the last one is a
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224 titanium plate for wavelength calibration.
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226 Since Curiosity’s landing in 2012, the calibration targets have been widely
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37 used, with more than 200 observations on each of them. The titanium plate
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39 is used the most frequently, every 14 sols (martian days), for wavelength
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228 calibration. Besides their role to validate the quantitative models developed
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42 from the terrestrial database [30], they have been used for the investigation
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230 of the dust composition [31], as well as for the investigation of LIBS physical
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45 effects, such as the signal obtained depending on the distance of the target
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47 [32, 33].
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234 What we learned from the ChemCam instrument operating on Mars since
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53 2012 is that optimal on-board standards should meet the following require-
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235 ments: mechanical integrity (i.e. low porosity and ability to survive launch,
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237 space and landing environments); low surface roughness; identical physical
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11 238 matrix; homogeneity of texture and composition, and wide range of compo-
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13 239 sitions. For example, it is best to select calibration targets that are homo-
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15 240 geneous both chemically and texturally throughout their surface in order to
16
17 241 obtain the same signal independent of the sampling location on the target.
18
19 242 Also, rough opaque surfaces are better than smooth transparent ones to avoid
20
21 243 any problem with surface adsorption of the laser photons, needed to create
22
23 244 a LIBS plasma. Matrix effects are also important in LIBS and it is desirable
24
25 245 to have a similar physical matrix for all the targets [34, 35, 36].
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246 **3. Geological Calibration Targets**

247 *Perseverance's* landing site is a 50-km diameter impact crater which is
248 located on the North West edge of Isidis Basin and North East of the Syrtis
249 area region, in one of the unique carbonate-bearing geological units detected
250 on Mars [37]. Jezero is a Noachian-aged crater, that is interpreted to be
251 an open-basin lake system, with two inlet valleys and one outlet valley [38,
252 39, 40]. Some remnants of fluvial deltas flank the crater rim's interior. The
253 western delta is to be explored during the prime mission [41]. Jezero's total
254 watershed area has been estimated at more than 10 000 Km² [38, 42], meaning
255 that deposits found in Jezero can be sourced from the units around, which
256 is very important for the overall context.

257 After multiple mapping efforts [38, 43, 44, 45], several units with different
258 mineralogies have been distinguished in orbital data [37, 46, 47]. The salient
259 mineralogies correspond to phyllosilicates, i.e. Fe-Mg smectites, present in
260 the delta deposits and indicative of aqueous alteration [48], olivine/Mg-rich

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9 261 carbonates-bearing units [37] that have been detected inside the crater, but
10 262 also regionally outside the crater [38, 45, 49, 50, 51], a mafic mineralogy
11 263 (mainly high-Ca pyroxenes) mainly associated with the crater floor (but
12 264 also in the deltas and rim). There are several hypotheses as to how these
13 265 carbonate-bearing formed, either by serpentinization process or hydrother-
14 266 malism [37, 38, 47, 52, 53]. Marginal Mg-carbonate deposits have been ob-
15 267 served along the west inner rim of the crater. They show the strongest and
16 268 most diverse carbonate signature observed within the crater and may have an
17 269 origin related to the lacustrine activity [54]. Finally, impact mega-breccias
18 270 (with high-Ca pyroxene signatures) have also been detected on the western
19 271 crater rim, and some of the blocks inside could represent pre-Noachian ig-
20 272 neous crust, as it is interpreted to predate the Isidis basin formation [55].
21 273 Details about the mineralogy and stratigraphic relationships between units
22 274 can be found in [45]. In summary, Jezero crater is a unique place exhibiting
23 275 primary and secondary mineralogies, along with carbonate-bearing deposits
24 276 of intriguing origin. This site records the past environment of Mars, its
25 277 climate evolution, and therefore is of great interest in the search for biosig-
26 278 natures and organic compounds, *in situ* and for sample return.
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45 280 A set of 23 LIBS targets has been selected in order to fulfill both instru-
46 281 mental calibration needs and science objectives for the LIBS technique. The
47 282 list of the on-board calibration targets is given in Table 1, along with their
48 283 short description, their technical name and their position on the holder. The
49 284 convention for these technical names was as follows: 1) the length has to
50 285 be less than 10 digits; 2) first letter (except for Titanium and Shergottite)

Position	Target #	TargetName	Description	Science Intent
2.1	7	TSRICH0404	BHVO-2 basalt and K sulfate mixture	Sulfur detection
2.2	8	LCMB0006	Chert	Past aqueous environment and astrobiology interest
2.3	9	LCA530106	Calcite	Carbonate calibration
2.4	10	PMIFS0505	Ferrosilite	Stoichiometric reference
2.5	11	TAPAG0206	Fluoro-Chloro-Hydro Apatite	Volatile detection, phosphate
3.1	12	PMIOR0507	Orthoclase	Stoichiometric reference
3.2	13	PMIDN0302	Diopside	Stoichiometric reference
3.3	14	PMIFA0306	Olivine	Stoichiometric reference
3.4	15	PMIAN0106	Andesine	Stoichiometric reference
3.5	16	PMIEN0602	Enstatite	Stoichiometric reference
3.6	17	TSERP0102	Serpentine/Talc	Hydrated silicate, alteration product
4.1	18	LBHVO20406	BHVO-2 standard basalt	Mars analog, basaltic composition
4.2	19	LJSC10304	JSC-1 standard	Mars soil analog
4.3	20	LANKE0101	Ankerite	Carbonate calibration
4.4	21	LSIDE0101	Siderite	Carbonate calibration
4.5	22	LJMN10106	JMN-1 standard Mn nodule	Mn enrichment, coating detection
5.1	23	NTE010301	Basalt dopped in minor elements	Calibration and quantification of Cu, Zn
5.2	24	NTE020106	Basalt dopped in minor elements	Calibration and quantification of Mn, Ba, Cr
5.3	25	NTE030106	Basalt dopped in minor elements	Calibration and quantification of Zn
5.4	26	NTE040106	Basalt dopped in minor elements	Calibration and quantification of Li, Sr
5.5	27	NTE050301	Basalt dopped in minor elements	Calibration and quantification of Ni
5.6	28	SHERG02	Shergottite	ChemCam cal. target replicate, cross calibration
/	33	TITANIUM	Titanium	Wavelength calibration

Table 1: List of the SuperCam geological targets on-board *Perseverance*, with their position on the sample holder.

indicates the city of sample laboratory, or where the replicate was sintered (see part 4); 3) three to five characters for the proper name of sample; 4) two digits for the batch number for the sintering; 5) two digits for the replicate number. Among these 23 calibration targets, there is a titanium plate dedicated to the wavelength calibration just as for ChemCam. More details about this target can be found in [9]. The 22 geological targets are split into 5 groups depending on the science intent as well as the calibration purpose:

3.1. Primary Igneous Minerals

From the ChemCam experience, targets with well-known stoichiometric compositions (such as minerals) are needed in order to validate the prediction models that are developed from a laboratory database. Such stoichiometric

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10 297 compositions are useful to calibrate key elemental ratios including Al/Si,
11 298 (Fe+Mg)/Si, (Na+K)/Si, (Ca+Na)/Si, Na/K. From a LIBS perspective, the
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13 299 use of these ratios can check and potentially correct for matrix effects and
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15 300 variation in ablated mass, which is the prerequisite to realize robust calibra-
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17 301 tion curves. Moreover, they are used for geochemical comparison between
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19 302 measurements made on Mars and in the laboratory on Earth, and can assist
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21 303 in a mineralogical assessment of the martian sampled targets.

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23 304 To fulfill this need, several igneous minerals have been chosen: feldspars,
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25 305 olivine and pyroxenes, which are widespread on Mars both in igneous rocks
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27 306 but also in sedimentary rocks (mostly as detrital minerals). Igneous minerals
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29 307 involve various solid solutions between end-members: Na-Ca in plagioclase,
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31 308 Na-K in K-feldspar, Fe-Mg in olivine, and Ca-Fe-Mg in pyroxene. Due to
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33 309 the constraint concerning the number of targets, it was not possible to select
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35 310 all of the end-members. Also, a few of them would not have been relevant
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37 311 to the martian geology and therefore six igneous minerals have been care-
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39 312 fully selected. We made the following compromise in selecting them: a)
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41 313 three targets are solid solutions frequently observed on Mars ([56, 57] and
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43 314 references therein): orthoclase and andesine for feldspar solid solutions; and
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45 315 Forsterite₆₅ (Fo₆₅) for olivine. b) three pyroxene targets on the other hand
46
47 316 have been chosen close to end-member compositions: Ca-Mg (diopside), Mg
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49 317 (enstatite) and Fe (ferro-hypersthene). Within the pyroxene quadrilateral
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51 318 composition domain, the field covered by those three mineral compositions
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53 319 encompasses a majority of pyroxene compositions found in Martian mete-
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55 320 orites as well as by *in situ* analyses of ChemCam on Curiosity ([56, 57]).
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57 321 Also, the ferro-hypersthene plays an important role for the Fe quantification,
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9 322 as it represents the highest Fe content among the on-board calibration set.

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11 323 Jezero crater was thought before landing to have a mafic floor unit [37, 38,
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13 324 44, 45, 46, 47, 49]. Whether it does or not, it is important to have targets that
14
15 325 address igneous compositions. Observations at Gale crater suggest that much
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17 326 of Mars' sedimentary material may consist of fine-grained igneous material
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19 327 with varying amounts of clay matrix [58].

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21 328 All these targets correspond to natural crystals. The two feldspars are
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23 329 sourced from centimeter-sized single crystals. The plagioclase presents an
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25 330 andesine composition and comes from Purdy mine Ontario (Canada); the K-
26
27 331 feldspar with orthoclase composition is from Alto Ligonha in Mozambique.
28
29 332 Olivine Fo₆₅ has been extracted from polycrystalline aggregates (millimeter-
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31 333 sized crystals) within a dunite sample from Bushveld stratified complex
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33 334 (Australia) [59]. The pyroxenes (diopside, enstatite and ferro-hypersthene)
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35 335 are centimeter-sized single crystals that come respectively from the Ecole
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37 336 des Mines collection in Paris (France), from Andranondambo outcrop in
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39 337 Maromby (Madagascar) and from metamorphic rocks of Mansjöbeg südlich
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41 338 Los Härjedalenin (Sweden).

42 43 339 *3.2. Targets enriched in minor elements*

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45 340 The terrestrial laboratory database covers a wide range of compositions
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47 341 and rock types. Minor elements are also well covered. However, this database
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49 342 has been developed mainly to quantify the major elements, and therefore in
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51 343 these standards the trace/minor elements do not always permit the construc-
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53 344 tion of calibration curves or limit of detection (LOD) determination. Also,
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55 345 because many of these elements have relatively few emission lines, many of
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57 346 which are low in intensity, it is important to have a reference for LIBS spectra

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347 acquired on Mars.

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11 Five different targets have been selected to address this goal, being doped
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13 349 in several elements in various amounts: Li [10-80 ppm], Cr [500-3000 ppm],
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15 350 MnO [500-4000 ppm], Ni [500-5000 ppm], Cu [50-2000 ppm], Zn [1000-10000
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17 351 ppm], Rb [10-1000 ppm], Sr [50-1500 ppm], and Ba [50-2000 ppm]. The range
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19 352 and contents of these elements have been chosen based on ChemCam's ob-
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21 353 servations at Gale crater [60, 61] (Figure ??), and the expected geology to be
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23 354 encountered in Jezero crater, along with some laboratory investigations (this
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25 355 is the case for Ni). With such targets, the LOD on Mars of all these elements
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27 356 can be well identified, along with their quantification model. These trace
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29 357 and minor elements are of interest in terms of geological processes undergone
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31 358 by the analyzed rocks. Some are being used as clues for a magmatic history,
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33 359 others for water/rock ratios in sedimentary processes, or also to distinguish
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35 360 different meteoritic falls [62, 63]. These five targets have an overall basaltic
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37 361 composition. These, combined with the igneous mineral calibration targets
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39 362 and others, are useful to characterize targets of igneous composition and may
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41 363 help to study weathering processes in a sedimentary context.

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45 365 *3.3. Standard targets*

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47 366 Standard targets are interesting as their bulk chemistry can be used as
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49 367 Mars analog compositions. Three standards have been selected: a basalt
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51 368 (BHVO-2) Basalt, Hawaiian Volcanic Observatory [64], a Mars regolith ana-
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53 369 log (JSC Mars-1) [65], and a manganese nodule (JMn-1) [66].

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55 370 Concerning their calibration purpose, they all have a specific interest.
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57 371 First of all, they have very distinct chemical compositions, which are im-

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9 372 portant to encompass the chemical matrix effects that can be observed with
10 373 LIBS [67]. Also, the JSC-1 soil (Mars regolith) analog contains the highest
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12 374 TiO_2 content of the targets, which is important to validate the earth-based
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14 375 quantification model(s). The JMn-1 target is special due to its MnO con-
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16 376 tent, up to 30 wt%. This represents the highest MnO abundance among the
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18 377 SCCT and it helps constraining the prediction model(s), as high Mn val-
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20 378 ues may interfere with the iron predictions based on ChemCam experience.
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22 379 Targets with a Mn-rich coating have been sampled with ChemCam at Gale
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24 380 crater [17, 18], along with Mn-rich vein filling material and Mn-rich nodules
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26 381 [68]. This JMn-1 standard also has the highest Ni abundance among the
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28 382 targets, which is important due to the elevated LOD of this element. Those
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30 383 standards provide great insights concerning the past atmosphere on Mars, as
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32 384 Mn requires water and highly oxidizing conditions to precipitate as an oxide
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34 385 [69, 70]. On Earth, coatings are also related to some biological processes
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36 386 (microbes can colonize a pre-existing coating, or they can create the coat-
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38 387 ing themselves). Such targets are therefore of particular interest in terms
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40 388 of astrobiological potential of the planet, which is one of the main goal of
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42 389 the Mars2020 mission. The BHVO-2 basalt comes from the USGS collection
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44 390 and is considered as an analog for the martian basaltic floor, and could be a
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46 391 good reference to compare with data obtained on the mafic floor of Jezero.
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48 392 It comes from the pahoehoe lava from the Halemaumau crater within the Ki-
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50 393 lauea caldera, in Hawaii (USA) [64]. The JSC Mars-1 material comes from
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52 394 the Johnson Space Center and has been collected in a palagonitic tephra
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54 395 in the Pu'u Nene cinder cone in Hawaii (USA) [65]. The JMn-1 manganese
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56 396 nodule originates from the collection of the Geological Survey of Japan. This
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397 Mn-rich sample comes from the floor of the southern Central Pacific Basin,
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11 398 at a depth of around 5 Km below the water sea level [66].
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14 399 *3.4. Natural rocks*

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16 400 Natural rocks are part of the calibration data set, and correspond to five
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18 401 different targets: one chert, three carbonate-bearing rocks (limestones) and
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20 402 one serpentine/talc.

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22 403 For an instrumental point of view, these compositions fulfill the need of
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24 404 having a wide variety of rock types to minimize potential chemical matrix
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26 405 effects. These rock types are clearly different from each other, with lime-
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28 406 stones containing almost no Si and instead contain a significant amount of
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30 407 carbon in the form of carbonates, whereas the chert is almost pure SiO₂, and
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32 408 serpentine is a hydrated silicate. The quantification of the SiO₂ content in a
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34 409 relatively pure SiO₂ target is really fundamental, as for example amorphous
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36 410 silica (like opaline) is known to have a role in microbial fossils preservation
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38 411 [71] and therefore is of interest for astrobiological perspectives. Chert there-
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40 412 fore accounts for the Si-rich end-member for calibrations. The carbonates
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42 413 and chert correspond to end-members with respect to their SiO₂ and FeO
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44 414 content.

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46 415 Carbonate minerals have been observed in several locations on Mars and
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48 416 on Mars meteorites. However, most of the time their abundance is low, such
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50 417 as in Mars meteorites (<1 wt % [72]), or in the dust from orbital and *in situ*
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52 418 measurements [73]. *In situ* measurements revealed a carbonate-rich mate-
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54 419 rial at Comanche outcrop, explored by the Spirit rover (with up to 30 wt %
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56 420 of carbonates [74]). At Gale crater, only hints of carbonates have been de-
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58 421 tected [75], but siderite has been detected recently in the clay-rich unit [76].
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10 422 However, orbital data observed carbonate-bearing rocks at Jezero crater and
11 423 overall in the Syrtis area [37, 54], along with some hydrated silicates such as
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13 424 serpentine [52]. Carbonates may not be easy to discriminate with LIBS when
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15 425 they are mixed with other material [77, 78]. Also, carbon content has not
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17 426 been quantified for ChemCam, and the C lines observed in the spectra mainly
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19 427 come from the breakdown with the atmospheric CO₂ [77, 78]. Therefore, to
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21 428 better enable detection of carbonates with SuperCam, we have selected 3
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23 429 samples: calcite (Ca), ankerite (Ca, Fe, Mg) and siderite (Fe). The calcite
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25 430 comes from the Paleozoic “Lunel limestone” formation in the quarry of Fer-
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27 431 ques (northern France). The ankerite comes from the Dome Mine in Timmins
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29 432 in Ontario (Canada), and the siderite comes from Antler Mine in Mohave
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31 433 County, Arizona (USA). The Jezero crater carbonate-bearing rocks, observed
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33 434 through orbital data, correspond mainly to Mg-carbonates, exposed in differ-
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35 435 ent contexts [45, 54]. They are mainly spatially associated with olivine and
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37 436 serpentine [54, 79]. This assemblage suggests an *in situ* deposition, possibly
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39 437 a serpentinization product of the ultramafic igneous floor, even though this
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41 438 origin could also be detrital [38, 44, 79]. In this context, a serpentine has also
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43 439 been selected as a calibration target. The selected serpentine comes from the
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45 440 Jeffrey Mine in Quebec (Canada). However, after the sintering process and
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47 441 its exposure to high temperature (see part 4), the serpentine target structure
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49 442 turned into talc, but with no change in terms of elemental composition. [80].
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51 443 With both carbonate and serpentine (at least in chemical composition), the
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53 444 onboard calibration set contains both major products formed by olivine al-
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55 445 teration under aqueous conditions, although it does not contain iron oxides,
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57 446 which are also by-products.

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10 447 Finally, hydrated silica appears to be relatively common on Mars, as it
11 448 has been detected both from orbit and *in situ*. From orbit, it has been de-
12 449 tected in terrains from the Noachian to the Amazonian, all over the surface
13 450 in various geological settings, from hydrothermal origin [81], but also from
14 451 alteration processes [82, 83]. *In situ* observations of hydrated silica are also
15 452 numerous, in diverse environments as well. The Opportunity rover team de-
16 453 tected enriched silica (possibly hydrated) on the western rim of Endeavour
17 454 crater, mixed with some Al-rich smectite, suggesting an acidic diagenetic ori-
18 455 gin [19, 20]. The Spirit team also detected some enriched silica hypothesised
19 456 to be opaline silica formed by hydrothermal activity [21, 84, 22, 23], at Home
20 457 Plate. At Gale crater, Si-rich rocks were also detected in the forms of detrital
21 458 tridymite in mudstone suggested to come from silicic volcanism [24], and of
22 459 some amorphous silica in fracture halos [25], suggested to be opaline silica
23 460 from their hydration level [26]. Hydrated silica on Mars is an indicator of
24 461 past aqueous conditions of the planet (diagenetic or hydrothermal events). It
25 462 may also represent a particular interest in terms of astrobiological potential
26 463 [85, 86, 87], which is an important aspect for the Mars2020 mission.
27 464 As mentioned earlier, a chert target has been selected for the SuperCam cal-
28 465 ibration targets. This natural target ensures that SuperCam will correctly
29 466 quantify high SiO₂ abundances. The selected chert comes from the 3.46 Ga
30 467 Marble Bar Chert Member of the East Pilbara Craton (Western Australia)
31 468 [88].

3.5. *Synthetic targets*

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54 470 Taking into account all the targets presented above, some geochemical
55 471 elements and targets of interest are still missing in the on-board calibration
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10 472 dataset, such as sulfates, chlorides, and halogens. Therefore, some synthetic
11 473 targets have been specifically prepared in order to make sure that these ele-
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13 474 ments are present in these calibration targets and well detectable by Super-
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15 475 Cam at the different levels of concentration, allowing all science objectives
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17 476 to be addressed.

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19 477 Besides the hydrated silica mentioned earlier, remote-sensing and *in situ*
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21 478 observations have provided extensive evidence for the presence of other hy-
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23 479 drated minerals such as phyllosilicates and sulfates on Mars. These hydrated
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25 480 minerals are important for understanding Mars's climate and its past hab-
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27 481 itability. First, clear orbital signatures have shown the presence of Ca and
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29 482 Mg hydrated sulfates in light-toned layered sediments [89, 90]. Sulfates have
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31 483 now been observed from orbit in many different types of outcrops ([91] and
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33 484 references therein). Gale crater was chosen as the Curiosity landing site
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35 485 from orbital detection of a transition between clay-bearing to sulfate-bearing
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37 486 rocks, suggesting a significant change in climate [82, 92]. *In situ* analyses at
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39 487 Gale, approaching the sulfate-bearing unit capping Mount Sharp, revealed
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41 488 a vast network of Ca sulfate filling veins at certain regions [93, 94, 95], and
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43 489 most of them correspond to bassanite [96], even though anhydrite is also
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45 490 present ([97] and reference therein). Primary Mg sulfates were also detected
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47 491 more recently [98]. A sulfate-bearing calibration target was therefore im-
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49 492 portant to include with SuperCam, even if no sulfates have been identified
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51 493 within Jezero crater from orbit. Unfortunately, Ca and Mg sulfates were not
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53 494 possible to include in the calibration targets. Mg sulfates are hygroscopic,
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55 495 whereas the mechanical structure of Ca sulfates changes with temperature,
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57 496 along with their hydration state. These properties were not in accordance

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497 with the fabrication process chosen for the calibration targets, nor with the
498 validation steps needed for delivery at JPL [9]. As featuring a pure sulfate
499 calibration target was not necessary, the team decided to create a mixture
500 between a basaltic material and a non-hygroscopic sulfate material that is
501 also stable with temperature. The final choice was a mixture between the
502 BHVO-2 basalt (see above section), and a K sulfate called arcanite. Natural
503 arcanite is relatively rare on Earth and not really relevant for Mars geological
504 settings and past habitability, but it addresses the need of detecting sulfur-
505 bearing targets with SuperCam, as well as of validating the quantification
506 model.

507 Phyllosilicates are also extensively observed from orbit ([91] and refer-
508 ences therein). These hydrated minerals reflect a past environment where
509 water on Mars was abundant. Unfortunately, no phyllosilicate such as clay
510 minerals could be part of the calibration targets on-board, as their physical
511 properties made them fail all the mechanical tests [9] required for such flight
512 models. Therefore, such targets are only included in the laboratory database.
513 However, the serpentine represents an hydrated alteration product.

514 Apatite is an ubiquitous magmatic mineral found in SNC meteorites. It
515 is a significant reservoir of halogens in these meteorites and has been used
516 to estimate the halogen budget of Mars [99]. While apatites in Mars mete-
517 orites are mainly enriched in Cl and H [100, 101, 102], apatites identified in
518 sandstones and pebbles at Gale crater by ChemCam [103, 104] are F-rich.
519 Determining the composition of apatite-bearing Martian rocks is important
520 to understand the behavior of volatiles during planetary differentiation [101]
521 and apatite is an important mineral for geochronological dating. A wide va-

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9 522 riety of apatites, including possible hydroxyapatites, may thus be expected.
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11 523 Therefore, providing a synthetic fluorinated and chlorinated hydroxy-apatite
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13 524 as a calibration target appears especially pertinent. One apatite composition
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15 525 was selected to give a reference for P, Cl, F and H abundances. While Cl and
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17 526 F are important in order to estimate the halogen budget of the Martian man-
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19 527 tle, P and H are also relevant for organic detections. Besides its geochemical
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21 528 importance, this target is used as a reference for the detection of P, Cl, F
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23 529 and H, as this is the only target containing these elements, and having them
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25 530 well quantified. Since this is also the only phosphate, it will help validate the
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27 531 quantification model, and will be useful whenever P is present in significant
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29 532 abundance in a sample.

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31 533 Finally, the SuperCam calibration set also includes a “ChemCam repli-
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33 534 cate”, which is the ChemCam shergottite-composition synthetic glass cali-
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35 535 bration target [27]. It is used as a reference for cross-calibration between both
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37 536 instruments. It also represents a certain Martian rock type, as it is a basaltic
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39 537 shergottite that has a chemistry similar to Bounce Rock ejecta observed at
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41 538 Meridiani Planum and to basaltic shergottite EETA79001B [105, 106].

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44 540 We emphasize that SuperCam’s LIBS calibration targets should address
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46 541 the instrument’s purposes and also the science objectives of the mission.
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48 542 With that, SuperCam should be able to determine the igneous chemistry
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50 543 of the putative mafic floor, characterize the chemistry of the carbonates
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52 544 observed from orbit within and around, and therefore give insight to the
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54 545 relationship between the olivine and some of its alteration products such
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56 546 as serpentine or Mg/Fe carbonates along with some phyllosilicates. More-

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10 547 over, these calibration targets help identify diagenetic products (for example
11 548 Mn/Fe oxides, Si-rich deposits), and also aid the search for biosignatures
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13 549 thanks to their content in specific elements such as Mn, Cl and the C, H, N,
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15 550 O, P, S.
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18 551 **4. Fabrication Process**

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21 552 The choice of the fabrication process for the SuperCam LIBS Calibra-
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23 553 tion targets has been driven primarily by the lessons learned from Chem-
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25 554 Cam. ChemCam’s calibration target assembly [27, 28, 29] was composed
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27 555 of two types of material: glassy targets to simulate igneous compositions,
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29 556 and some pressed powders sintered at 800 degrees C with a small amount
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31 557 of lithium tetraborate to simulate Mars sediments. However, the synthetic
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33 558 silicate glasses had a different physical matrix than igneous rock (resulting
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35 559 in physical matrix effects that have hindered their use in calibration), and
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37 560 the sintered material were quite heterogeneous at the scale of the laser beam
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39 561 [36].

40 562 Given that background with ChemCam, a renewed effort was made to
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42 563 produce more representative and more homogeneous on-board targets for Su-
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44 564 perCam. Homogeneous targets are easiest to produce by vitrifying crushed
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46 565 powder. However, it is well known that the laser-matter interaction during
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48 566 ablation can be significantly different on glass and on crystalline material, as
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50 567 they have different optical properties as well as physical properties such as
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52 568 hardness. Powder pellets obtained by conventional uniaxial pressing would
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54 569 be usable for all the SuperCam spectroscopies, but such pellets cannot han-
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56 570 dle the mechanical and thermal constraints induced by launch and landing.
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571 Natural rocks are generally more robust, but they are rarely homogeneous
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572 at the sub-millimeter resolution of the SuperCam techniques, due to the
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13 573 mineral-grain distribution. Therefore, with all these constraints, the choice
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15 574 was to make most targets by a sintering process, using a flash consolidation
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17 575 technique, namely the Spark Plasma Sintering (SPS) process. Only three
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19 576 targets have not been sintered (titanium, shergottite and chert - see below).
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23 578 The SPS technique is a sintering process involving high pressure along
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25 579 with an electrical current passing through the powdered sample [107, 108]. It
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27 580 is a well known way to significantly improve the mechanical properties of the
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29 581 sintered samples compared to usual pressing techniques [109]. This technique
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31 582 reaches a better density and compaction for a wide range of materials, and
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33 583 improves the bonding quality [110] thanks to a mechanical grain-to-grain
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35 584 rearrangement, the growth of the finest grains and lattice dislocation. In
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37 585 that way, sintered pellets have no risk of outgassing in vacuum (or under
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39 586 Mars environment) and have mechanical properties that are in accordance
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41 587 with NASA requirements [10]. The effect of heat has been investigated in
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43 588 different matrices and even though some mineral phases may be modified,
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45 589 no important bulk chemical changes or reduction in homogeneity have been
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47 590 noticed after SPS [10]. Also, [111] have shown the high repeatability of the
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49 591 technique. The added value and quality of such a technique is discussed in a
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51 592 large number of studies cf. [112]. The SPS technique is fast, as it takes only
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53 593 a few minutes to sinter materials. The overall process consists in using fine-
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55 594 grained powders. This powder is placed into a graphite die in a treatment
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57 595 chamber that may be put under vacuum or a controlled atmosphere (*e.g.*

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10 596 argon). A pulsed current is then applied, and passes through the sample via
11 597 electrodes and the conductive die. At the same time, a uniaxial mechanical
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13 598 pressure is applied to the die for a few minutes. Both current and pressure
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15 599 are then released (this step being controlled if needed). The sample is then
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17 600 left to cool down for a few minutes.

18
19 601 The SPS process has been performed by two laboratories: Mateis labo-
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21 602 ratory, INSA, Lyon (France) using an SPS HP D25 machine (FCT®), Ger-
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23 603 many), and CIRIMAT laboratory (PNF2 national CNRS platform) in Toulouse
24
25 604 (France), using an SPS Sumitomo Dr Sinter 2080 apparatus. Two different
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27 605 methodologies were used. In Lyon, for each composition, one pellet of 40
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29 606 mm diameter was made and then cored to extract 6 pellets of 10 mm each
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31 607 in diameter. As it is known to have a thermal gradient from the center to
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33 608 the edge of the sample [111], the 6 cores have been extracted from the same
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35 609 distance from the center. On the other hand, in Toulouse, for each compo-
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37 610 sition, 6 individual pellets of 11 mm in diameter each were fabricated. The
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39 611 pellets were then slightly ground in order to remove any graphite from the
40
41 612 die, and to adjust the diameter to 10 mm. The machining process was per-
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43 613 formed either at Société Audoise de Précision (SAP) in Ambres (France) or
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45 614 at SCERAM™ in Lyon (France), with no oil and no water to avoid any
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47 615 contamination of the samples. Table 2 gives the detailed parameters for each
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49 616 target, from Lyon and Toulouse.

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51 617 Only the standard targets (BHVO-2, JSC-1, JMn-1) were purchased in
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53 618 the form of powders, while, for all the other selected targets, several steps
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55 619 had to be performed before the sintering.

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57 620 The igneous minerals were coarse single crystals that experienced slow

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Target	Description	SPS conditions		
		Temperature (Celcius)	Pressure (Mpa)	Duration (min)
PMIEN060x	Enstatite	1375	100	3
PMIOR050x	Orthoclase	1150	100	5
PMIAN010x	Andesine	1200	100	3
PMIFSI050x	Ferrosilite	1050	100	3
PMIFA010x	Forsterite	1150	100	10
PMIDN030x	Clinopyroxene	1200	100	3
NTE01030x	Trace elements	800	75	3
NTE02010x	Trace elements	800	75	3
NTE03010x	Trace elements	800	75	3
NTE04010x	Trace elements	800	75	3
NTE05030x	Trace elements	800	75	3
LCA53010x	Calcite C53	750	75	3
LJSC1030x	Mars soil sim.	750	75	3
LBHVO2040x	Basalt	1000	75	3
LJMN1010x	Mn-rich	750	75	3
TAPAG030x	Apatite	950	50	5
LANKE010x	Ankerite	750	75	3
LSIDE010x	Siderite	750	75	3
TSERP010x	Serpentine	750	100	3
TSRICH040x	S-rich	1000	100	3

Table 2: SPS parameters (temperature, pressure, and duration of constraints) used for each of the sintered LIBS SCCTs.

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9 621 cooling to reach such a size (mm-cm). As temperature decreased, exsolution
10 622 lamellae may be formed within some of the crystals. Therefore, it was nec-
11 623 essary to crush them down to fine powders (grain size smaller than average
12 624 exsolution lamellae) to produce mechanically and chemically homogeneous
13 625 samples. The grain size of the powders is estimated to be less than 50 μm .
14
15 626 After this grinding step, the SPS technique was performed as referred in
16
17
18 627 Table 2.

19
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21
22 628 The natural targets (chert, carbonates, serpentine) were natural rocks
23 629 that have been finely crushed, the same way as the igneous minerals, with
24 630 grain sizes below 50 μm before the SPS process. The sintering process was
25 631 attempted on the chert. This rock, mainly composed of SiO_2 quartz, yielded
26 632 crumbly pellets by SPS at low temperatures. The sintering was successful
27 633 only above 1700°C by melting SiO_2 [10]. The pressure and temperature the
28 634 sintering process were thus similar to those of chert formation. In the end, we
29 635 used chert in its original state, after coring the main rock to get six samples
30 636 from it.

31
32 637 The minor-doped targets were produced the same way as the glassy
33 638 ChemCam calibration targets [27]; they were synthesized by mixing pow-
34 639 ders of carbonates, silicates, oxides and sulfates in order to get the same
35 640 bulk composition for the six replicates done for each doped targets, adding
36 641 minor and trace elements as listed above. These mixtures went through sev-
37 642 eral melting, cooling, and crushing cycles in order to obtain a homogeneous
38 643 glassy material. The actual composition of the synthetic silicate glasses was
39 644 then checked by LA-ICP-MS measurements in order to make sure the desired
40 645 major-element composition along with the minor/trace element contents was

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646 reached. This glassy material was then crushed one last time prior to per-
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647 forming the SPS process.

648 Concerning the sintered targets, each sample followed its own specific
649 process. The sulfur-rich target (TSRICH) is simply a mixture of 30 % of the
650 BHVO-2 standard powder with 70 % of the arcanite (K sulfate) commercial
651 powder, before being sintered.

652 The ternary F, Cl, OH-apatite target was synthesized in full at CIRIMAT,
653 Toulouse. The aim here was to prepare an apatite phase simultaneously
654 containing OH⁻, F⁻ and Cl⁻ ions in the hexagonal crystal structure. Two
655 F⁻OH⁻apatite and Cl⁻OH⁻apatite precursor powders were first obtained by
656 tuned fluorination and chlorination, respectively, starting from stoichiometric
657 OH⁻apatite. The process was carried out in a tubular furnace under argon
658 flow (1 atm) in the temperature range 900-950°C, and NH₄F or NH₄Cl were
659 selected as halogen reagents. The sublimation/decomposition of these com-
660 pounds led to gaseous HF and HCl molecules able to partially dehydroxylate
661 the OH-apatite. The F⁻OH⁻apatite and Cl⁻OH⁻apatite precursor powders
662 were then mixed (for 4 hours) in the desired proportions selected to produce
663 the targeted F, Cl, OH composition. Electron microprobe analyses have been
664 performed in order to check if the desired composition was achieved. Then,
665 the sample was sintered as presented in Table 2. The sintering process ap-
666 plied to this apatite target was different to that of the other targets in two
667 respects. First, the applied mechanical pressure was slightly lower than that
668 of other targets. But most importantly, the sintering process was carried un-
669 der Argon (instead of vacuum) in order to minimize the loss of Cl. This led
670 to a ternary F, Cl, OH apatite phase corresponding to the chemical formula

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671 $\text{Ca}_5(\text{PO}_4)_3(\text{OH}_{0.08}, \text{F}_{0.49}, \text{Cl}_{0.43})$ as assessed by electron microprobe analyses.

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673 Finally, for the shergottite ChemCam replicate [27], in order to avoid
674 any contamination or change in composition during crushing and the SPS
675 processes, this sample was only cored to the right size directly from the
676 replicate. As it is a glassy material, this process was tricky and we were
677 able to get only two samples with the correct dimensions from the material
678 remaining from ChemCam. Finally, the titanium target is a plate from a
679 commercial supplier [9], and as mentioned above, the Chert (natural target)
680 was cored directly from the rock.

681 **5. Spectral characterization of the geological samples**

682 In this section we use qualitative observations to investigate the homo-
683 geneity of the targets. Quantitative compositions will be given in Section
684 6.

685 *5.1. Geological Targets' Homogeneity to LIBS*

686 Targets that are dedicated to the LIBS technique are used as references
687 once on Mars. It is therefore of prime importance to characterize them in
688 terms of homogeneity (chemical and mineralogical) in order to make sure that
689 each pellet presents a homogeneous elemental spatial distribution, and that
690 each replicate (the one on-board Perseverance and the others on different
691 labs) is similar for every given composition. A summary of all the techniques
692 used for each target and replicate is presented in Table 3. This section is
693 only a short summary of [80], and therefore details with tables and figures
694 can be found in [80].

Target Name	Description	EMPA	LA-ICPMS	XRF and microRaman	LIBS in Spain	LIBS in France	SuperCam-like Raman	VISIR in Canada	VISIR in France
TSRICH040x	BHVO-2 basalt and K sulfate mixture	None	None	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
LCMB000x	Chert	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
LCAS3010x	Calcite	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
PMIF5050x	Ferrosilite	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
TAPAG020x	Fluoro-Chloro-Hydro Apatite	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
PMIOR050x	Orthoclase	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
PMIDN030x	Diopside	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
PMIFAD30x	Olivine	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
PMIAN010x	Andesine	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
PMIEN050x	Enstatite	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
TSERP010x	Serpentine/Talc	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
LBHVO2040x	BHVO-2 standard basalt	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
LUSC1030x	JSC-1 standard	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates (including FM) but FS	Lab replicate	CR replicate	Lab replicate
LANKE010x	Ankerite	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
LSIDE010x	Siderite	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
LJMN1010x	JMN-1 standard Mn nodule	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
NTE01030x	Basalt doped in minor elements	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
NTE02010x	Basalt doped in minor elements	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
NTE03010x	Basalt doped in minor elements	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
NTE04010x	Basalt doped in minor elements	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
NTE05030x	Basalt doped in minor elements	All replicates	FM and FS replicates	All replicates	CR replicate	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate
SHERG0x	Shergottite	All replicates	FM and FS replicates	All replicates	None	All replicates but FM and FS	Lab replicate	CR replicate	Lab replicate

Table 3: Summary of all characterization techniques used on the calibration targets. FM, FS and CR replicates stand for Flight Model, Flight Spare and Calibration Replicate, respectively. EMPA and LA-ICP-MS have always been performed on the bottom of the targets. Quantitative results from those techniques will be given in Section 6

Different techniques have been used to evaluate the homogeneity of the calibration targets: μ XRF "mapping" for the elemental spatial distribution, continuous Raman spectroscopy imaging for the structural variability and mineralogical heterogeneity, and LIBS individual analysis for a more sensitive comparison to our needs. More details concerning these different methodologies can be found in [80].

XRF and Raman analyses were performed at the University of Basque Country in Bilbao (Spain). Concerning the μ XRF technique, sixteen single-spot analyses (4×4 grid), with a pixel resolution of $25 \mu\text{m}$, were done to simulate a single $100 \mu\text{m}$ analysis. A total of 10 randomly distributed spots were therefore analyzed on each sample and each replicate was analysed the same way. The homogeneity was evaluated by averaging the 10 spots, and calculating the relative standard deviation ("RSD" in %) for each element detected. The distribution of the elements was considered homogeneous when

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9 709 the RSD was lower than 10 %, quasi-homogeneous when RSD was between
10 710 10 and 20 %, and heterogeneous when RSD is higher than 20 %. This homo-
11 711 geneity gradation concerns only the major constituents, as minor elements
12 712 that are present at less than 1 wt% can display higher RSD values.

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17 713 Raman hyperspectral mapping was used to check the target structural
18 714 and mineralogical homogeneity. For this technique, a 532 nm continuous-
19 715 wave laser was used with the same wavelength as the SuperCam instrument.
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22 716 The analyzed spectral range was 100-3200 cm^{-1} . All replicates of each target
23 717 have been mapped.

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26 718 LIBS measurements were made at IRAP in Toulouse (France), as well as
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28 719 at University of Malaga (Spain). Measurements in Toulouse were acquired
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30 720 using the ChemCam laboratory unit [4, 5, 113, 96], which is very similar to
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32 721 the Flight Model onboard Curiosity. The mast unit is placed in a climatic
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34 722 chamber at -10°C in order to get the best energy for the laser. The spot size
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36 723 on the target was around 300 μm at 1.5 m from the instrument. More details
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38 724 about the setup can be found in [96]. Nine random points of 30 shots were
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40 725 performed on 4 of the replicates (Flight Model and Spare were preserved).
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42 726 Samples were placed in the Mars chamber, filled with 6 mbar of Mars-like
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44 727 atmosphere (95.7 % CO_2 , 2.7 % N_2 , 1.6 % Ar). LIBS spectra were then
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46 728 processed using the same methods as the Mars ChemCam spectra [114].

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48 729 LIBS analyses in Malaga were performed using a laboratory LIBS setup
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50 730 that was tuned in order to have similar characteristics as the ChemCam
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52 731 setup. The main difference is the spot size that is slightly bigger (350 μm).
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54 732 For each target, eleven sampling points were distributed over an inner cir-
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56 733 cumference of 6.0 mm in diameter: 9 points of 30 shots to evaluate surface

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10 734 homogeneity and 2 of 90 shots to evaluate the in-depth homogeneity. Tar-
11 735 gets were placed under a Mars-similar atmosphere (only CO₂) at 7 mbar, at
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13 736 a distance of 1.5 m. Only one replicate was sampled by LIBS for each target
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15 737 in Malaga.
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19 739 *XRF mapping.* Most of the targets have a homogeneous distribution of
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21 740 their major elements, with RSD less than 10 %. However, the JSC Mars-1
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23 741 target (regolith analogue) and the JMn-1 target (Mn nodule) present some
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25 742 chemical heterogeneity, but only for elements below 2 wt% in content (Na₂O,
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27 743 K₂O, TiO₂). This heterogeneity observed for the minor elements is not a
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29 744 special concern, as the JMn-1 target has been specifically chosen for its high
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31 745 Mn content, which is seen very homogeneous by XRF. More details about
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33 746 the methodology and results can be found in [80].

34 747 *Raman imaging.* The SuperCam calibration targets have been estab-
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36 748 lished mainly for LIBS analysis purposes, and therefore some of them are
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38 749 not easily characterized by the continuous-wave laser Raman spectroscopy
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40 750 used for these homogeneity investigations. This is the case for the targets
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42 751 enriched in minor elements as they are amorphous materials. As previously
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44 752 discussed, during the sintering process some targets have shown a mineralog-
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46 753 ical transformation including phase transition [10]. It was the case of siderite
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48 754 (Fe carbonate), which led to a calcite and magnetite mixture; and of ankerite
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50 755 (initially containing some silicates) that changed into calcite and quartz. For-
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52 756 tunately, the mineral targets (Andesine, Diopside, Enstatite, Olivine, and
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54 757 Orthoclase), as well as the calcite, the chert, and the sulfate-rich target
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56 758 (TSRICH) were not transformed into another phase and are mineralogically

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10 759 homogeneous according to the Raman imaging done on the entire surface
11 760 of the targets. Additionally, several targets were confirmed to be homoge-
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13 761 neous in terms of structure and mineralogy at micro scale, and could clearly
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15 762 be used as reference for the Raman technique as well once on Mars. More
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17 763 details about Raman characterization of the targets can be found in [80].

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19 764 *LIBS analysis.* In Spain, LIBS analysis was performed on one replicate
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21 765 of each calibration target. The LIBS spectra have been processed and the
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23 766 net intensity has been retrieved for some elemental lines, in order to cal-
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25 767 culate their RSDs. Taking into account the RSDs obtained [80], only the
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27 768 TSRICH target was considered as heterogeneous for some major elements.
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29 769 Nevertheless, as the purpose of that target is to monitor its sulfur signal
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31 770 (that could not be detected in Malaga's set up), this overall heterogeneity is
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33 771 not such a concern. Moreover, its S content was classified as homogeneous
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35 772 from the XRF results. Then, to a lower extent, three other targets showed
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37 773 some heterogeneity, but only for one element each and with the RSD always
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39 774 below 30 %. In France, several mathematical treatments were used on the
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41 775 LIBS spectra to check the homogeneity of the targets. In order to do so,
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43 776 the elemental lines of interest (major elements of each target) were fitted in
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45 777 order to get their peak areas. First, the GINI Index [115] was calculated
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47 778 from these peak areas. A GINI index below 0.25 means the target is consid-
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49 779 ered homogeneous, between 0.25 and 0.5 it is fairly homogeneous, and above
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51 780 0.5 it is heterogeneous. Using this technique, only the TSRICH target was
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53 781 again identified as heterogeneous (GINI index at 0.6). All the other targets
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55 782 have a GINI index below 0.25 for all their major elements [80]. Additionally,
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57 783 the RSD has been computed from the peak areas. Again, the TSRICH tar-

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9 784 get presents the highest variability with a RSD around 26% for sulfur peak,
10 785 which was acceptable given the difficulty to fit the S line. Two targets were
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12 786 fairly heterogeneous: JSC and TSERP, which is consistent with the previous
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14 787 LIBS study. The homogeneity has been also checked using some Independent
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16 788 Component Analysis [116, 117, 118] and only the TSRICH target showed a
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18 789 heterogeneous result.
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23 791 Finally, coupling all these techniques to investigate the homogeneity of
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25 792 the targets with LIBS, it has been concluded that only the TSRICH target
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27 793 was heterogeneous at the LIBS spatial scale for most of the elements, besides
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29 794 SO₃ and K₂O that represent more than 70 wt% of the target. Therefore,
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31 795 heterogeneous elements in this sample do not constitute a major part of the
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33 796 target. LIBS analyses have shown that all the other targets are homogeneous
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35 797 at the LIBS scale (300µm, corresponding to the laser beam size), which is
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37 798 the main purpose of this work. The detailed results about homogeneity of
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39 799 the targets can be found in [80].
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41 800 5.2. VISIR Spectra of geological targets

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43 801 VISIR spectra were acquired in two laboratories, the University of Win-
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45 802 niipeg (Canada) and the Institut de Planétologie et d'Astrophysique de Greno-
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47 803 ble (IPAG) at Université Grenoble-Alpes (France). Different replicates of the
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49 804 calibration target materials were used in each laboratory, and the separate
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51 805 spectral acquisition methods are described below.
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55 807 At the University of Winnipeg, reflectance spectra were collected with a
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57 808 Malvern-Panalytical Analytical Spectral Devices (ASD) LabSpec 4 Hi-Res
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9 809 reflectance spectrometer. This ASD spectrometer consists of three separate
10 810 detectors that cover the 350–1000 nm (Si photodiode array), 1000–1830 nm,
11 811 and 1830–2500 nm (InGaAs detectors with moving gratings) intervals. A
12 812 single 2 m long fiber optic cable was used to collect the reflected light from
13 813 samples. This cable consists of 44 separate silica fibers with internal diam-
14 814 eters of 200 μm each. The full diameter of the bundle was 1.85 mm. This
15 815 fiber optic cable was fed to an optical scrambler that ensured light from each
16 816 fiber was combined and equally fed to all three optical paths that fed the
17 817 detectors. The Si photodiode array was then fed by a fiber optic bundle
18 818 consisting of 19 separate 100- μm diameter silica fibers. The two InGaAs de-
19 819 tectors were fed by separate fiber bundles consisting of 9 separate 200- μm
20 820 diameter silica fibers. These offsets were removed by multiplicatively scaling
21 821 the low (350–1000 nm) and high (1830–2500 nm) wavelength portions of the
22 822 spectrum to the middle portion. The instrument has a spectral resolution
23 823 that ranges between 3 nm for the photodiode array and 6 nm for the InGaAs
24 824 detectors. Dark currents were removed from all spectra during correction
25 825 to reflectance. These spectra were corrected for the absorption properties
26 826 of the Spectralon reflectance standard, but were not corrected for the non-
27 827 Lambertian behaviour of Spectralon. An in-house light source was used for
28 828 illumination that consists of a quartz-tungsten-halogen (QTH) bulb illumi-
29 829 nating a set of reflectors that feed the light through a pipe at a divergence
30 830 of <1.5 degrees. The filament was operated at a temperature that provided
31 831 sufficient output over the 350-2500 nm range. The measured spot was cen-
32 832 tered close to the center of the SCCT targets. Spectra were collected on the
33 833 “unpolished” side of each target, even though it was done prior to the 9 LIBS

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9 834 point analysis.

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13 836 At IPAG laboratory, reflectance spectra of SCCTs were measured at IPAG
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15 837 using the Shadows instrument [119]. We used the standard mode of the in-
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17 838 strument (around 7 mm diameter illumination spot) and spectra were mea-
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19 839 sured under nadir illumination and using an observation angle of 30° (phase
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21 840 angle= 30°). Spectra were normalized to Spectralon and Infragold and cor-
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23 841 rected for the non-lambertian behavior of spectralon [120]. Spectra were
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25 842 acquired at a 10 nm sampling in the 400–4200 range, with a spectral resolu-
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27 843 tion of 4.8 nm (<670 nm), 9.7 nm (670–1300 nm), 20 nm (1300–2500 nm)
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29 844 and 40 nm (2500–4200 nm).

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31 845

32 846 The calibration targets acquired in laboratories with some of the most
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34 847 useful VISIR spectral signatures are shown in Figure 2. The RMI Red color
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36 848 target exhibits strong visible-wavelength “red” slopes whereas the Cyan tar-
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38 849 get shows a major band centered near 1460 nm. Among the geologic targets,
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40 850 chert shows a hematite-like visible spectrum (with a peak near 750 nm fol-
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42 851 lowed by a strong downturn), resulting from minor hematite in the sample.
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44 852 The pyroxenes (Ferrosilite, Enstatite, and Clinopyroxene) exhibit character-
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46 853 istic bands in the 2000 nm region whose centers depend on Fe/Mg content
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48 854 and mineral structure [121]. Calcite includes signature bands near 2340 nm
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50 855 and 2530 nm. The orthoclase has few spectral features, except for a notable
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52 856 increase in reflectance toward shorter visible wavelengths. Finally, the Ser-
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54 857 pentine spectra exhibit a similar “blue” slope in the visible, hydration bands
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56 858 near 1400 nm 1910 nm, and a major band near 2312 nm and minor bands

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10 near 2291 nm and 2391 nm that reflect contributions from both serpentine
11 and talc (e.g., [122]). SuperCam VISIR spectra acquired from Mars are also
12 shown for comparison in Figure 2. Even though these preliminary spectra
13 are slightly more noisy, the same spectral features can be observed.
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18 5.3. Raman Signature

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20 Remote time-resolved Raman spectroscopy (SuperCam-like) spectra have
21 been acquired at Institut de minéralogie, de physique des matériaux et de cos-
22 mochimie (IMPMC) of Sorbonne Université in Paris (France), with a Remote
23 sensing and time-resolved Raman spectrometer in a SuperCam-like config-
24 uration. The remote configuration of a customized time-resolved Raman
25 and luminescence spectrometer built at IMPMC was used for the present
26 study [123, 124]. Relying on a conventional Schmidt-Cassegrain telescope
27 (Celestron-C8 202 mm diameter Schmidt plate), this instrument allows
28 analysis of the Raman and luminescence signals by using time-resolution
29 spectroscopy. The laser is a nanosecond pulsed 532 nm DPSS laser (1.2 ns
30 FWHM, 1 mJ per pulse) with a 10 to 2000 Hz repetition rate. The fine
31 control and synchronization of both time delay and gating time of the ICCD
32 allows sub-nanosecond time resolution experiments. For the present study,
33 the laser beam was collimated at the sample surface (at 8 m from the tele-
34 scope Schmidt plate) on a spot of ~ 6 mm in diameter, with an irradiance
35 on the sample of about $\sim 10^{10} \text{W.m}^{-2}$ similar to that of SuperCam [124]. The
36 Raman signal was collected by the telescope from a surface with slightly
37 lower diameter than the co-aligned incident laser beam (field of view of the
38 optical fiber of about 4.5 mm at 8m). A notch filter was used to cut off the
39 Rayleigh scattering below 90 cm^{-1} and the signal was collected by an op-
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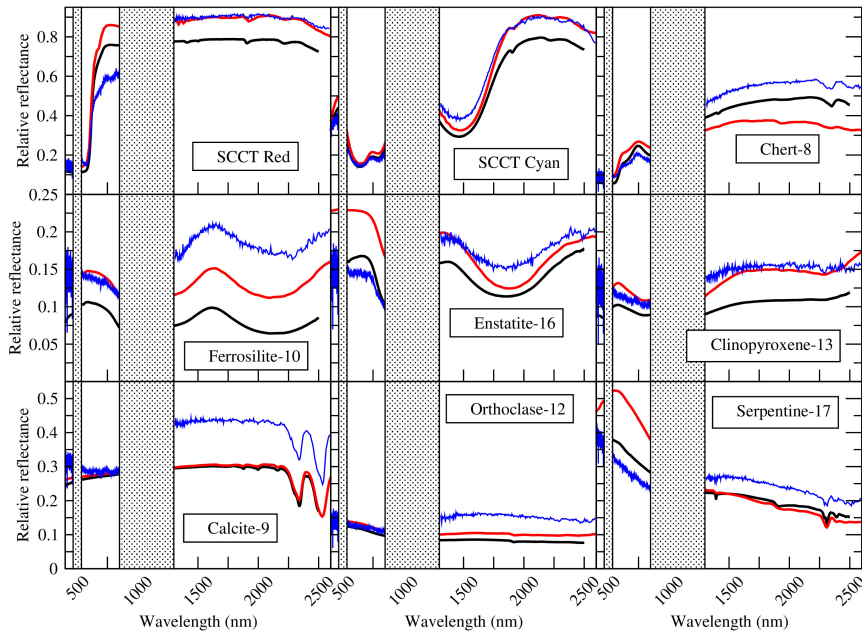


Figure 2: Laboratory and Mars spectra of SuperCam calibration targets that exhibit useful spectral features in the 400-2600 nm wavelength range (cf. Figure 1, Table 1). Spectra in black were acquired at the University of Winnipeg, and those in red were acquired at IPAG, Université Grenoble-Alpes. Blue spectra are those acquired on Mars. Stippled boxes represent regions where SuperCam does not collect data. All laboratory spectra were acquired at normal incidence and 30° emission angle. Differences in overall reflectance may occur owing to inherent differences in the target samples used by the different laboratories, and/or differences in corrections for the non-Lambertian nature of the Spectralon reference material (see text).

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10 884 tical fiber and sent into a modified Czerny-Turner spectrometer (Princeton
11 885 IsoPlane 320) coupled with an intensified Princeton PIMAX4 ICCD camera.
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13 886 This spectrometer has three motorized gratings that can be selected depend-
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15 887 ing on the spectral window and spectral resolution requested for the analysis.
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17 888 Here we used the 600 lines/mm grating yielding a spectral resolution of 10-13
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19 889 cm^{-1} similar to that of SuperCam. Here, we collected the spectra by using
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21 890 a 5 ns ICCD gate centered on the laser pulse. In order to maximize the
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23 891 signal-to-noise ratio, we accumulated the signal corresponding to hundreds
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25 892 of thousands of laser shots.

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29 894 Not all the geological targets show a clear signal using remote time-
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31 895 resolved Raman spectroscopy. This can be due to their mineralogy, but
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33 896 also their structure and texture (*e.g.* grain size). For example, all the
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35 897 minor-doped targets are amorphous material and time-resolved Raman spec-
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37 898 troscopy is not sufficiently sensitive to this material. Figure 3 shows a spec-
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39 899 trum of all the targets that present the best signal: these are the calcite, the
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41 900 apatite, and the Sulfur-rich targets.

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43 901 In the case of calcite, both internal (712 and 1087 cm^{-1}) vibrational
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45 902 modes and external lattices modes (282 cm^{-1}) are clearly observed. In the
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47 903 other carbonates, ankerite and siderite, only the most intense CO_3 internal
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49 904 symmetric stretching mode ν_1 at $1085\text{--}1090 \text{ cm}^{-1}$ is clearly detected. Simi-
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51 905 larly, in apatite, the principal internal symmetric stretching mode ν_1 of PO_4
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53 906 is observed at 960 cm^{-1} as well as other peaks corresponding to other inter-
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55 907 nal vibrations of the PO_4 group. Last, the sulfur-rich target exhibits several
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57 908 peaks corresponding to the internal modes including an intense one at Ca,

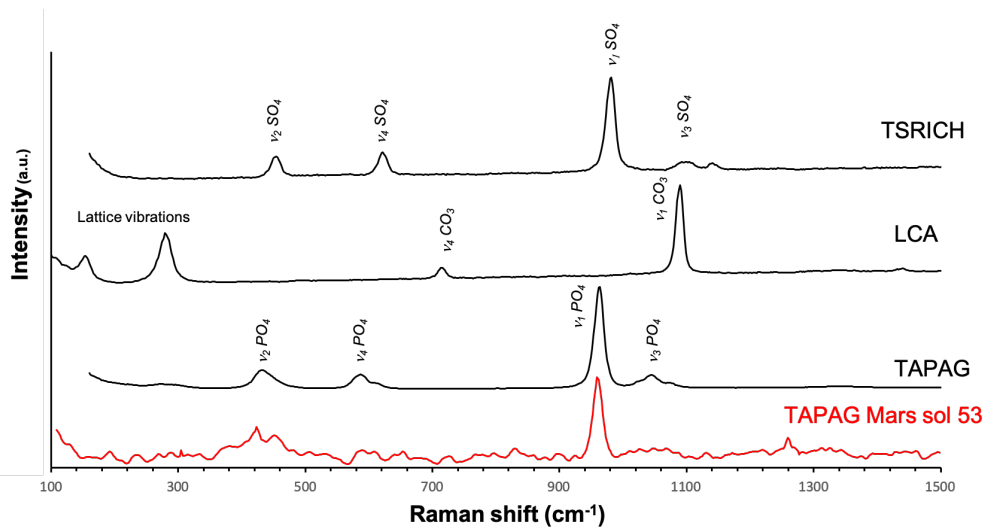


Figure 3: Time-resolved Raman spectra acquired remotely in a SuperCam-like configuration on the Apatite, Calcite and Sulfur-rich "TSRICH" calibration targets (in black). Spectrum of the apatite acquired on Mars is shown in red for comparison.

909 while the 1000-cm^{-1} line corresponds to the SO_4 internal symmetric stretch-
 910 ing mode ν_1 . The rover paint (not shown) is also interesting as it has a strong
 911 Raman signature with several bands at frequencies lower than 1000 cm^{-1} .

912 Since landing, Raman on SCCT has been used a few times, but only
 913 on the Apatite and Ertalyte (organic) targets. Figure 3 shows the apatite
 914 spectrum acquired on Mars as well. The apatite spectrum shown here was
 915 measured with 100 laser shots. The resulting spectrum is satisfying. The
 916 SNR is lower compared to the laboratory spectrum but this is likely due
 917 to the much lower number of laser shots used on Mars. However the main
 918 internal symmetric stretching mode ν_1 of PO_4 is clearly observed at 960 cm^{-1}
 919 as well as some other internal modes.

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9 920 *5.4. LIBS Spectra*

11 921 One complete set of replicates (CR) were analyzed at Los Alamos National
12 Laboratory (LANL) in New Mexico (USA) during the calibration campaign,
13 922 using the FM BU and the EQM MU [2, 3]. They were placed at 1.56 m
14 923 from the instrument (some of them were also sampled at 2.86 and 4.25 m),
15 924 under Mars atmosphere (7 Torr of CO₂). The instrument was placed in a
16 925 cold chamber, at -15°C. However, we present here only the spectra acquired
17 926 on Mars for more clarity. The average LIBS spectrum obtained for some
18 927 targets is presented in Figure 4 from UV to near infra-red, normalized to the
19 928 total intensity. Only a few targets are presented for clarity, to visualize the
20 929 diversity of signal obtained from one target to another.
21 930

22 931 The bottom spectrum, in dark blue corresponds to the calcite sample, where
23 932 only Ca emission lines are observed (along with weak C lines and O, from the
24 933 atmosphere). The ankerite, which is also a carbonate, is shown just above,
25 934 in light blue. Along with the intense Ca peaks, the Fe and Mg emission lines
26 935 are observed. The TSRICH target (in orange) is unusual, as it is a mixture
27 936 between a basalt BHVO-2 and the K sulfate. Therefore, all the major ele-
28 937 mental lines are observed, with huge K lines. Sulfur lines are weak compared
29 938 to others and therefore are shown in a close-up (Figure 5).

30 939 BHVO-2 (pink in Figure 4) has a basaltic composition and therefore all major
31 940 elements are present, with a complex LIBS signal. Orthoclase and Andesine
32 941 targets (dark and light green, resp.) show mainly emission lines produced
33 942 by alkali elements, Si, Ca and Al. Orthoclase shows higher K lines com-
34 943 pared to the andesine. The apatite target (purple) has one of the highest
35 944 Ca emission lines, and its spectrum in the UV (240-340 nm) and VIO (380-

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9 470 nm) ranges is quite flat except for these peaks (such as for the calcite).
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11 945 However, its Tspec spectrum shows a clear CaF molecular band. Figure 5
12 946
13 947 also shows its Cl and P emission lines. This target is the unique one with
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15 948 such elements. Finally, the chert presents significant emission lines from only
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17 949 two major elements, Fe and Si. However, Fe is one of the elements with the
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19 950 highest number of emission lines, mainly in UV and VIO.
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21 951

22 952 The targets doped in minor and trace elements show a wide range of
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24 953 signal concerning Sr, Rb, Cr, Li, and Ba due to their different doping in each
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26 954 of them (see section 3.2). This can be observed in the LIBS spectra in Figure
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28 955 6), where they are shown with no offset in order to highlight their diversity.
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30 956 Unfortunately, no Ni peaks are detected in these targets, which suggests
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32 957 that their content is below the LOD. However, all the other minor and trace
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34 958 elements are clearly observed, with the signal intensity being consistent with
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36 959 the doping of each of these targets, as seen in Table 5.
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39 960 **6. SCCT compositions**

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42 961 Access to actual compositions of all the replicates is a necessity, as these
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44 962 targets will be used to check the quantitative models performed from the
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46 963 terrestrial database [30, 15, 16].
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50 965 All the targets were analyzed with quantitative techniques in order to get
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52 966 their reference compositions for major and minor elements (Table 3. Electron
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54 967 Microprobe Analyses (EMPA) were performed at the micro-characterization
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56 968 center of Raimond Castaing, Université Paul Sabatier in Toulouse (France)
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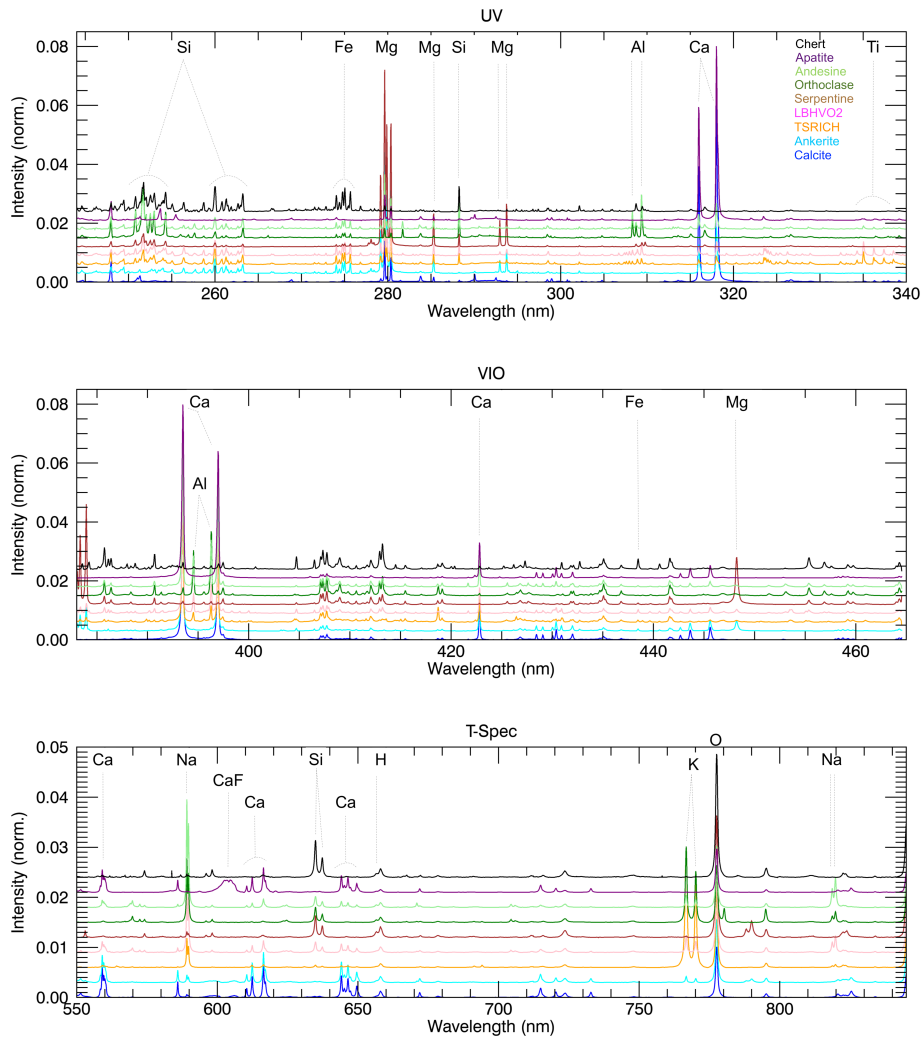


Figure 4: LIBS spectra (from UV to T-spec range) obtained on some of the SCCTs on Mars. Only a few examples are shown, to illustrate the diversity in LIBS signal.

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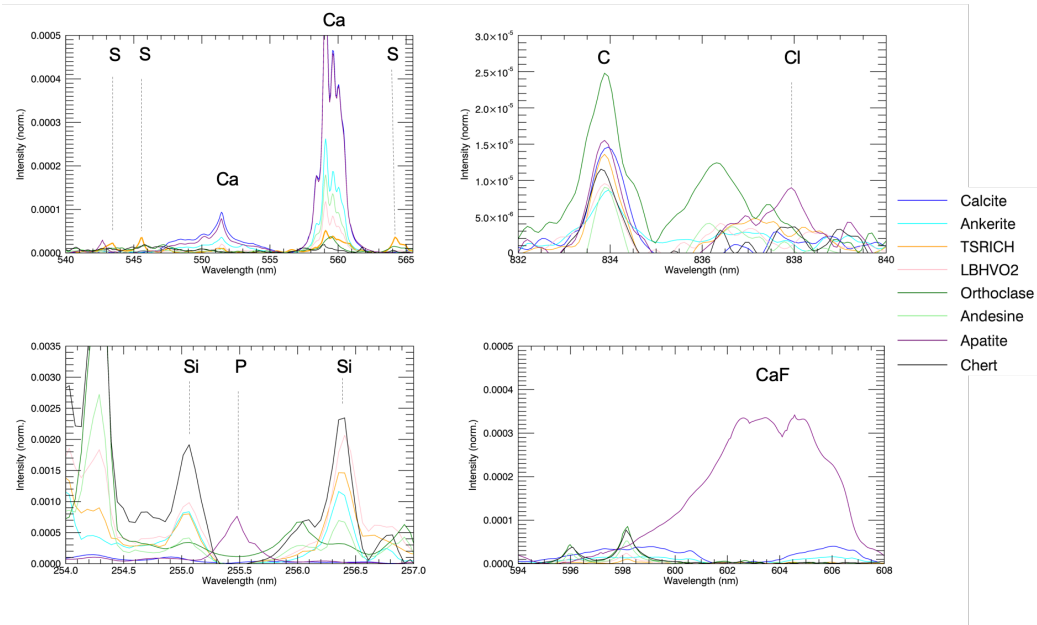


Figure 5: Close-up of some LIBS spectral portions to show specific signatures, particularly for the apatite (purple) and TSRICH (orange) targets.

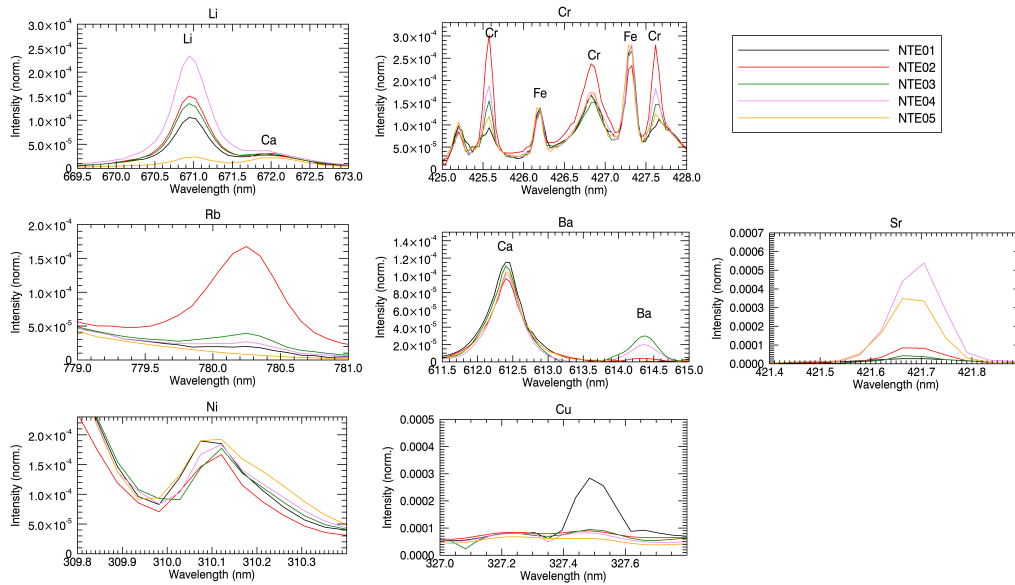


Figure 6: Close-up of spectral regions of the minor-doped targets for: Li, Cr, Rb, Ba, Sr, Ni, and Cu ranges.

and the Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS) measurements were performed at IStEP, ALIPP6 platform in Sorbonne Université in Paris (France).

The electron microprobe measurements were performed with a Cameca SXFive model. All the six replicates for each calibration target were analyzed, on the back of the target to prevent the surface. The analysis of all the six replicates was important in order to get the composition of all of them, and to make sure they were similar (because one is on-board, and the others are distributed in collaborating laboratories). The uncertainties of the EMPA technique are given in supplementary material, Table S2. To be consistent with the future LIBS analysis, and considering that the LIBS spot

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10 981 size is around 250 μm , microprobe analyses were done over 3 random squares
11 982 of $100 \times 100 \mu\text{m}$ with a 2 μm analysis spot size. In each square, nine point
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13 983 analyses were performed. 10 to 15 manually selected points were performed
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15 984 as well, in order to make sure that all the different phases were sampled at
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17 985 least once. Thus, a total of 37 to 42 points were analyzed on each replicate.
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19 986 The average composition of the replicate was calculated from the average of
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21 987 the mean value calculated from each random square and from each series of
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23 988 10–15 points. The standard deviation is calculated from these four averages.
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25 989 Finally, the RSD, used to assess the homogeneity of the sample, is calculated
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27 990 from the average composition and the standard deviation of the sample. This
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29 991 methodology gives a worst case scenario for the homogeneity compared to
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31 992 data from the LIBS analyses.
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34 994 The LA-ICP-MS measurements were performed with a “QQQ” technique
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36 995 or triple quadrupole mass spectrometre (8800 Agilent), coupled with an ab-
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38 996 lation laser excimer 193 nm (Teledyne Analyte G2).The advantage of the
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40 997 triple quadrupole mass spectrometer is to strongly limit the isobaric inter-
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42 998 ferences (oxides MO^+ and double charged M^{++}) due to the coupling with
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44 999 the laser ablation. Indeed, the passage of ions through two successive mass
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46 1000 spectrometers, allows a doubled selection. We performed analyses along 8
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48 1001 lines of 1 mm, with a laser spot size of 200 μm . These lines give a better
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50 1002 assessment of the composition (major and minor elements) than individual
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52 1003 points. This technique is more sensitive for the detection of trace and minor
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54 1004 elements than EMPA, but also the spot size is closer to the LIBS spot size.
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56 1005 Thus LA-ICP-MS results will give a better comparison with LIBS data. As
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1006 previously checked by EMPA, all the replicates for each sample are similar
11 [80] [see appendix], and therefore only the back of the Flight and Spare model
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13 1008 replicates were analyzed with this technique. The average composition and
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15 1009 the RSD obtained for each sample correspond to the average and deviation
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17 1010 calculated on the 8 analyzed lines.
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21 1012 All the flight targets (except one, see below) were analyzed both with the
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23 1013 EMPA and the LA-ICP-MS techniques. Figure 7a shows the major element
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25 1014 compositions obtained for the flight targets from both techniques. Most of
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27 1015 the points plot on the 1:1 line (in red), showing the very good agreement be-
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29 1016 tween the two techniques. Some analyses are farther away from the 1:1 line
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31 1017 and correspond mainly to the standard targets (triangles) and natural targets
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33 1018 (diamonds). However, when looking at the RSDs obtained from each quan-
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35 1019 titative technique (Figure 7b), these targets have much higher RSDs from
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37 1020 the microprobe technique compared to those from the LA-ICP-MS/MS. We
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39 1021 will conclude that this result is mainly due to the difference of the fields of
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41 1022 view (2 μm compared to 200 μm) relative to the size of the grains/minerals
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43 1023 constituting the sample.
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46 1025 This section will describe the differences observed between the two quan-
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48 1026 titative analyses, followed by the final compositions of the Flight Model cal-
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50 1027 ibration targets.

51 52 1028 *6.1. Standard targets*

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54 1029 Among the 23 SCCTs, three of them correspond to standards: BHVO-2
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56 1030 (basalt - [64]), JMn-1 (Mn nodule - [66]) and JSC-1 (Mars soil analogue -
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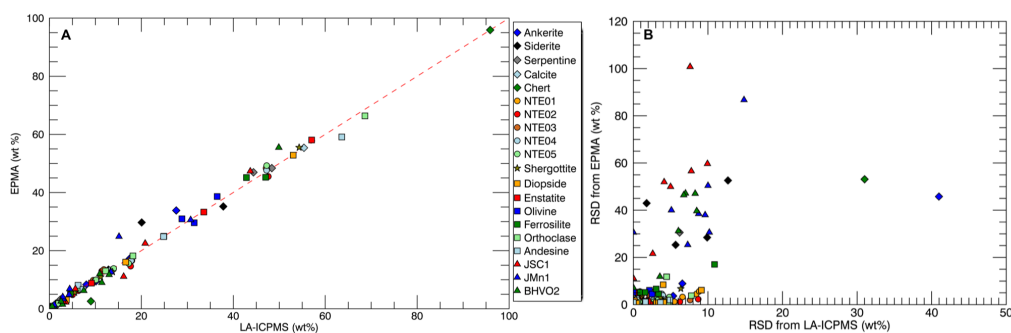


Figure 7: Comparisons of the results obtained between microprobe and LA-ICP-MS techniques. All major elements are shown here (SiO_2 , TiO_2 , Al_2O_3 , FeO , MgO , Na_2O , K_2O). Left: EMPA composition versus LA-ICP-MS compositions for all of the LIBS SCCTs. Right: RSDs obtained from the EMPA analyses vs RSDs obtained from the LA-ICP-MS analyses, for all major elements. RSD values represent the average scatter from the average composition obtained for the three squares and the 10 to 15 independent points; for the LA-ICP-MS results, RSD represents the variations of the average obtained from the eight scan lines.

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9 1031 [65]) samples.

11 1032 We observed some discrepancy for these targets between the EMPA and
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13 1033 LA-ICP-MS analyses, as seen in Figure 7a. Moreover, from the EMPA tech-
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15 1034 nique, RSDs from the accepted values can be as high as 60 % whereas with
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17 1035 LA-ICP-MS the RSDs are much lower, less than 10 %. The reason is ex-
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19 1036 plained below, for each of the standard target.

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21 1037
22 1038 Concerning the BHVO-2 target (green triangles in Figure 7), RSDs from
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24 1039 the EMPA results go up to 50 % for most of the major elements. Indeed,
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26 1040 Figure 8a shows a Back-Scatter Electron detector (BSE) image of this tar-
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28 1041 get (on the left), where at least 3 different phases can be easily detected:
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30 1042 plagioclase (darker grains), pyroxene and olivine (brighter grains). The or-
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32 1043 ange cross represents the EMPA spot size, which is clearly smaller than these
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34 1044 three different mineral types, therefore explaining this high heterogeneity and
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36 1045 the deviation to the composition deduced from EMPA compared to LA-ICP-
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38 1046 MS/MS. Moreover, black areas between the grains represent voids, signifying
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40 1047 that the surface state was not perfect. This is probably due to the presence
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42 1048 of multiple phases in that sample; the polishing of the surface was difficult as
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44 1049 many grains were being excavated during this process. The presence of these
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46 1050 voids can affect the quality of the quantification, as they return a biased
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48 1051 composition. The composition obtained from LA-ICP-MS is however in very
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50 1052 good agreement with the known reference composition (Figure 9b).

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53 1054 Concerning the JMn-1 standard (blue triangles in Figure 7), a BSE image
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55 1055 is shown in Figure 8b. Dark areas of more than 30 μm wide are observed

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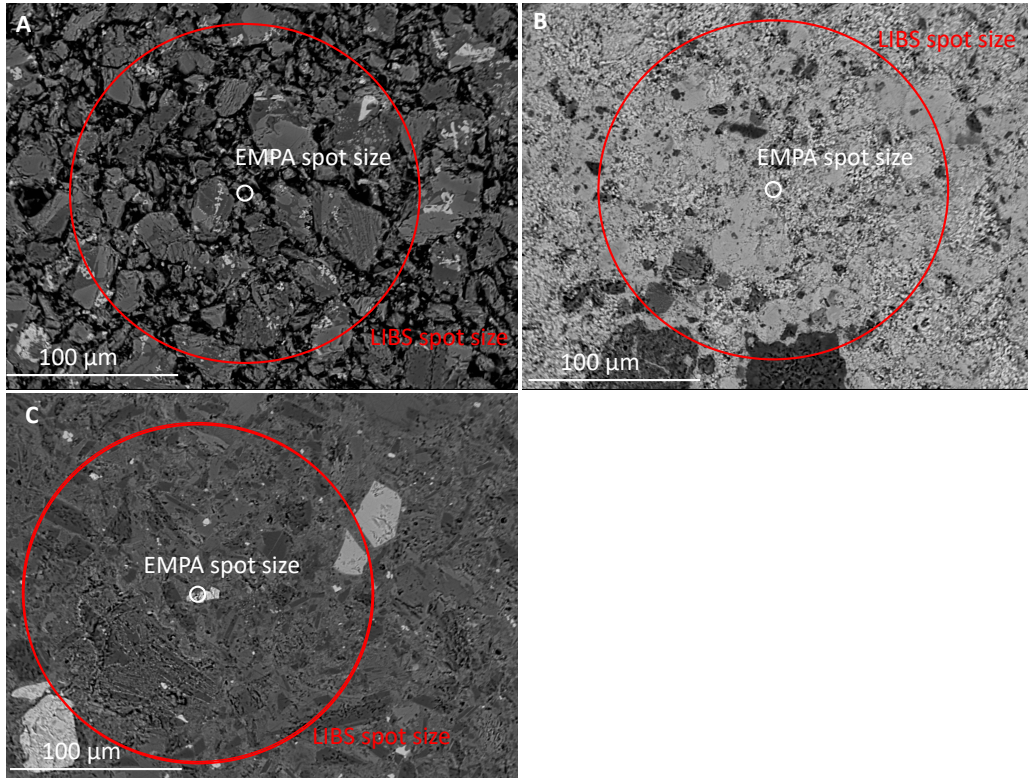


Figure 8: BSE images obtained on the Flight target of: A/BHVO-2; B/JMn-1; C/JSC-1. White circle represents the microprobe spot size, and red circle represents the LIBS spot size.

and correspond to quartz and feldspars. Even though the silicate phases are the most present, lots of very small bright grains are observed, which correspond to Fe or Mn oxides (this sample being chosen for these Mn oxides). When considering all the data points from the EMPA's predictions (Figure 10), we can observe a good agreement with the BSE image. Mn oxides are widespread, along with some Fe oxides, and these Mn oxides are enriched in Cu and Ni. Some feldspars can be detected as the SiO₂ is mainly correlated with Al₂O₃ and alkalis, even though some pure quartz has been

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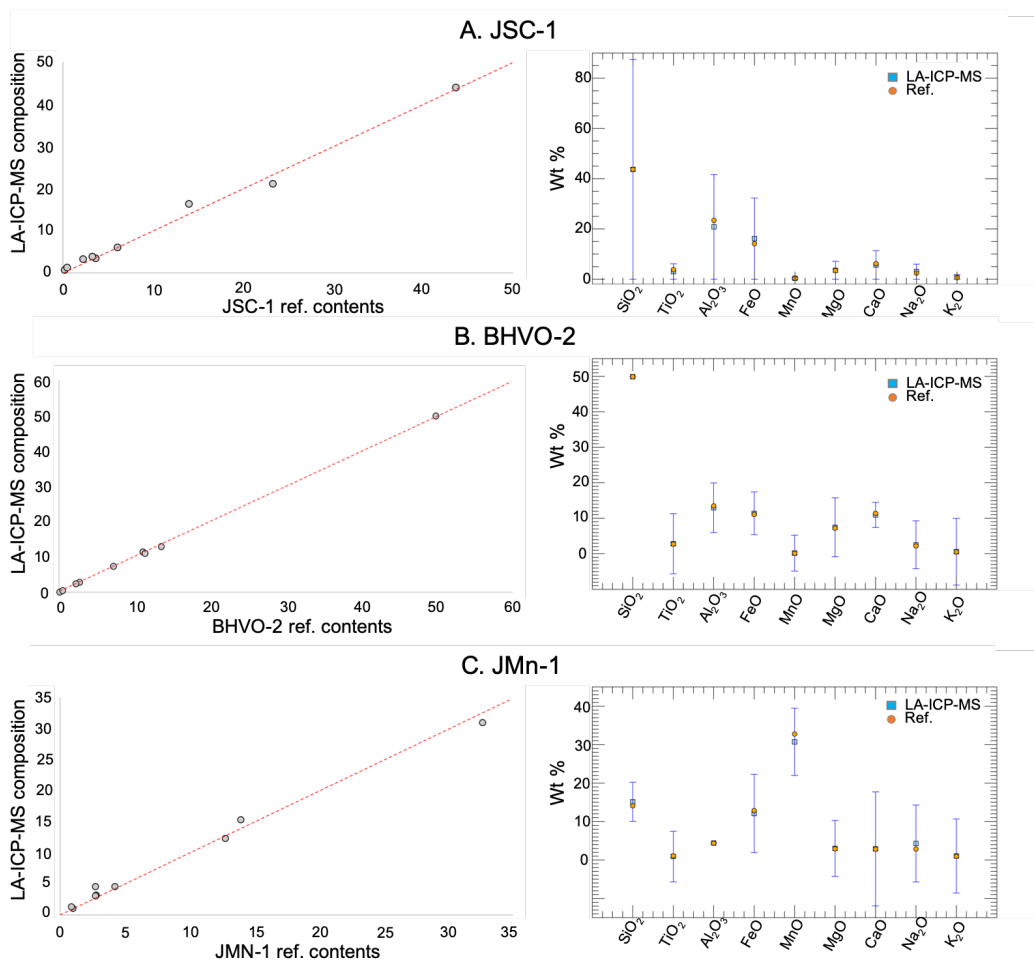


Figure 9: Comparison between compositions obtained from LA-ICP-MS on the Flight Model replicate and from their reference compositions. A. JSC-1 standard; B. BHVO-2 standard; C. JMn-1 standard. In the left column, red dashed line correspond to the 1:1 line. In the right column, the blue error bars correspond to the RSDs obtained from LA-ICP-MS/MS. Reference values come from [66] for the JMn, [64] for BHVO-2, and [65] for JSC. Details can be found in Table S1

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9 1064 sampled (but still quite rare). This reveals at least four different phases in
10 1065 this sample, most of them giving a sum of oxides far from 100 wt %. These
11 1066 observations can explain the higher Si content (25 wt%) obtained from the
12 1067 EMPA technique compared to the result from the LA-ICP-MS (15 wt %
13 1068 SiO₂), that is more representative of the bulk. The EMPA technique, even
14 1069 though performed with 40 to 50 points on this specific target emphasizes this
15 1070 heterogeneity that is clearly linked to the poly-crystallinity of that sample,
16 1071 with a high abundance of Mn oxides.
17 1072 Due to its larger spot analysis, the LA-ICP-MS results are more consistent
18 1073 with the bulk composition. Figure 9c shows the comparison with its reference
19 1074 composition [66]. Most elements are on the 1:1 line, even though a few small
20 1075 differences can be observed mainly for the SiO₂ and MnO contents, and to
21 1076 less extent for Na₂O and FeO contents. However, the reference composition
22 1077 is within the variations observed in the LA-ICP-MS measurements.
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38 1079 The JSC-1 standard (red triangles in Figure 7) differs mainly about its
39 1080 iron content that is higher from the LA-ICP-MS compared to the EMPA
40 1081 results (17.9 wt % for 11 wt %, resp.), but this is the target with the highest
41 1082 dispersion for all its major elements from the EMPA analyses. In LA-ICP-
42 1083 MS/MS, its RSDs are acceptable, lower than 10 %. The variability observed
43 1084 in EMPA is mainly explained by the presence of Fe and Ti oxides in that
44 1085 sample, that are clearly observed on the BSE image (Figure 8c, bright small
45 1086 grains) and the EMPA analyses. The LA-ICP-MS composition are more rep-
46 1087 resentative of its bulk, even though some differences are observed from the
47 1088 reference composition (Figure 9a). The main differences concern the Al₂O₃
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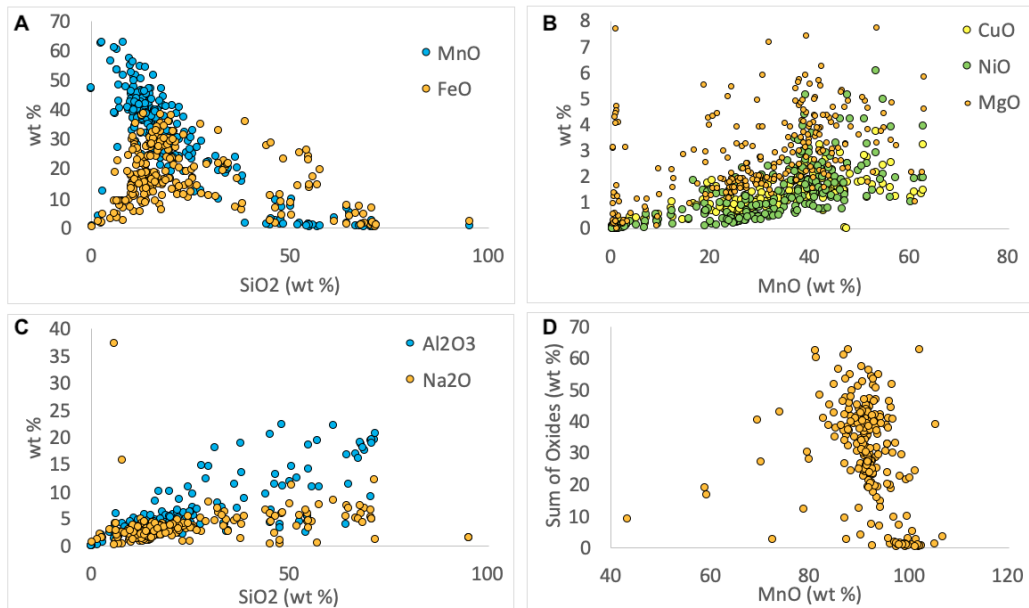


Figure 10: EMPA results obtained for JMn. All the 35 points are shown, for several elements. High values of MnO and FeO are observed for low SiO₂ content. These high Mn locations are also enriched in Ni and Cu.

1089 and FeO contents, but the variations observed in LA-ICP-MS data are larger
 1090 than the difference between our measurement and the reference value.

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1092 The JMn-1 target is the worst sample in terms of chemical quantification,
 1093 which was expected as this sample was chosen for its content of Mn oxides,
 1094 whereas BHVO-2 and JSC-1 samples also show much more variability than
 1095 expected in terms of mineral phases. That is why only the LA-ICP-MS val-
 1096 ues are reported in Table 4, as the scanning lines are more representative of
 1097 the bulk chemistry for these poly-crystalline targets. Comparison of the LA-
 1098 ICP-MS quantifications for these targets with their reference values (Figure
 1099 9) reveals that they are really close to each other, reinforcing our choice for

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1000 the LA-ICP-MS technique for these particular targets. The table of com-
1010 positions from the literature and from LA-ICP-MS is shown for these three
1020 standards in the supplementary material (Table S1).

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1040 Figure 11 from LA-ICP-MS data shows that the major elements for these
1050 standard targets (represented by triangles) have a RSD < 10 %, except for
1060 the JMn-1 with the CaO that has a RSD at 14.8 %. However, with RSD
1070 <15 %, these targets are homogeneous at the LA-ICP-MS scale. Even the
1080 minor elements of these targets have RSD overall <15 %, except Cr that is
1090 up to 40 %. JSC-1 has 0.1 wt % of Sr (RSD 8.8 %), JMn-1 contains 0.18 wt
1100 % of Ba (RSD 12 %), 1.47 % Ni (RSD 9.7 %), 1.35 % Cu (RSD 10.4 %), and
1110 0.1 % Zn (RSD 11.6 %).

1120 *6.2. Natural rocks*

1130 Among the natural targets (calcite, ankerite, siderite, serpentine and
1140 chert), the ankerite, siderite and chert have LA-ICP-MS results that differ
1150 from the microprobe ones, as can be observed on Figure 7a (diamonds).

1160 The ankerite and siderite have LA-ICP-MS and EPMA results that differ
1170 mainly for their CaO content, which is higher in microprobe than in LA-
1180 ICP-MS (33 wt % vs 27.6 wt % for ankerite, 29.6 wt % vs 20 wt % for
1190 siderite, Table 4). In the case of the siderite, the two techniques also differ
1200 for the FeO content, which is higher in LA-ICP-MS/MS. Their RSDs are also
1210 clearly higher from the EMPA analyses, even for the main element of these
1220 samples. These differences in composition and variability are also related to
1230 several phases in these samples. The siderite shows from the EMPA analyses
1240 (Figure 12a) that at least three different phases have been sampled: Fe ox-

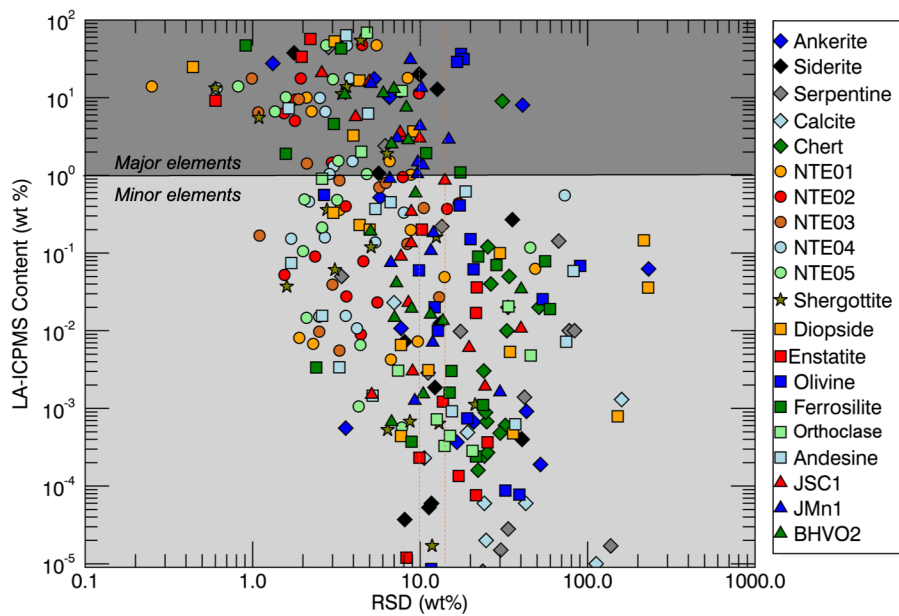
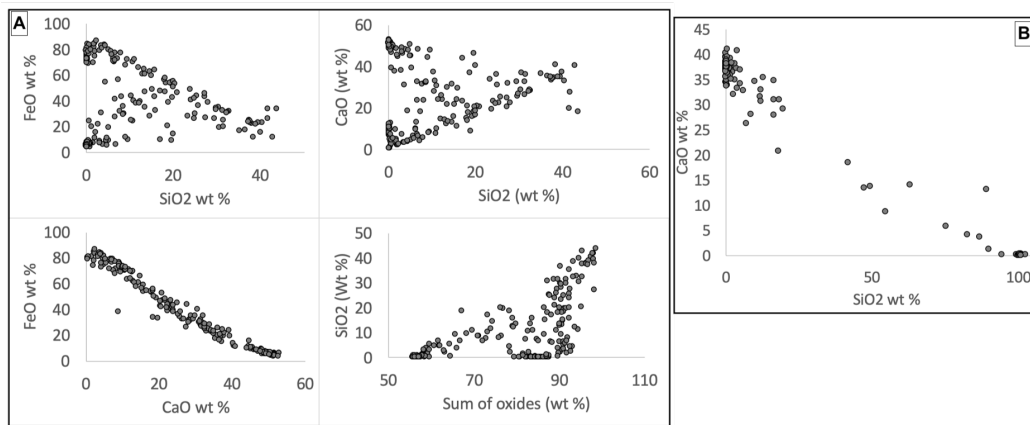


Figure 11: RSDs obtained from the LA-ICP-MS technique depending on the elemental content. All quantified major and minor elements are shown (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, Si, Li, Rb, Cr, Ba, Ni, Cu, Zn). Red dashed vertical lines correspond to 10 % and 15 % RSD for clarity.

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 1125 ides, a silicate phase, and a calcite. This can be explained by two factors: i)
 1126 the siderite chosen is not pure, *i.e.* it contains some silicates; ii) during the
 1127 flash-sintering process, the siderite mineral dissociated to become calcite with
 1128 some Fe oxides. This phenomena is explained in [10], and the consequences
 1129 are also observed in the Raman signal for that target [80]. Concerning the
 1130 Ankerite, high RSD is observed for SiO₂ only, as observed by both techniques
 1131 (even though lower in LA-ICP-MS/MS). EMPA data show that this target
 1132 actually contains some quartz grains (Figure 12b), as observed with Raman
 1133 as well [80].



44 Figure 12: Microprobe data obtained in the siderite (A) and in ankerite (B).

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 1135 The chert is the only target that is not from a sintering process. Therefore
 1136 some impurities and variations in composition are possible. Its LA-ICP-MS
 1137 and EMPA data differ (Figure 7, green diamond), especially regarding its
 1138 iron content, which was expected as the Marble bar chert has a lot of jas-
 1139 par bands running through it 13. This target, almost pure SiO₂, contains

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1140 a significant amount of FeO with an elevated RSD (31 % from LA-ICP-MS
1141 vs 53 % from EMPA - Figure 7b). EMPA data, due to the very small scale
1142 analysis, revealed some points enriched in FeO, and low in SiO₂ (Fig 13).
1143 The FeO content is too low to come from a sampling of pure Fe oxides (<
1144 30 %), but is anticorrelated with all other possible elements (as shown with
1145 SiO₂). Moreover, the BSE image shows very small bright spots (<1µm) that
1146 correspond to Fe oxides and that are scattered all over the target surface.
1147 Therefore these higher abundances in FeO in some points correspond to some
1148 mixtures between the chert and Fe oxides, too small to be sampled individ-
1149 ually even with the EMPA technique. This explains the overall lower FeO
1150 content (but higher RSD) obtained with the EMPA technique, compared to
1151 the results from LA-ICP-MS/MS. The LA-ICP-MS technique, with a bigger
1152 spot size and a scanning line, is more representative of the bulk composition.

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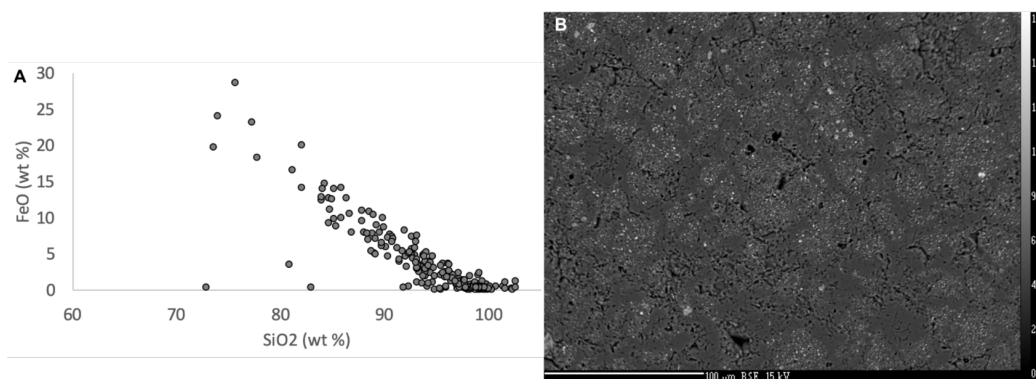


Figure 13: Microprobe data (FeO vs SiO₂) obtained in the chert (A) and BSE image of this target (B).

1154 Microprobe data for the calcite target show that it is almost entirely pure
1155 Ca carbonate, with no silicate or Fe oxides. RSDs are very low for the CaO

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9 1156 (< 3 %, Table 4). The CaO content is 55.4 wt %, which is stoichiometrically
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11 1157 consistent with a natural calcite. The CO₂ content can therefore be esti-
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13 1158 mated at 43.9 wt%. The CaO being the only major element of that target,
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15 1159 it was used as the internal standard for the LA-ICP-MS data normalization,
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17 1160 and therefore is not reported in Table 4.
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21 1162 The last natural target is the serpentine. Compositions from EMPA and
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23 1163 LA-ICP-MS are very close to each other (Figure 7 and Table 4), with RSD
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25 1164 values much lower from the LA-ICP-MS analyses. However, the main differ-
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27 1165 ence concerns the MgO content that is lower from the LA-ICP-MS compared
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29 1166 to EMPA (44.4 wt % compared to 46 wt % respectively), with comparable
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31 1167 RSDs (Table 4). This target is of great interest also for its H₂O content.
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33 1168 It has been measured using Thermal Gravity Analysis (TGA) technique at
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35 1169 IPAG (Grenoble, France) and estimated as well using the ChemCam-LIBS
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37 1170 technique, with the same methodology as the one developed in [96]. The wa-
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39 1171 ter content is between 1 and 3 wt% H₂O, which is consistent with the overall
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41 1172 composition obtained from LA-ICP-MS and EMPA (the sum of oxides is at
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43 1173 95-98 wt% from LA-ICP-MS and 100-102 wt% from EMPA, when taking
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45 1174 into account the H₂O content).
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47 1175 *6.3. Minor-element-enriched targets and shergottite*

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49 1176 These targets (NTE01, NTE02, NTE03, NTE04 and NTE05) show simi-
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51 1177 lar major-element results for LA-ICP-MS and microprobe analyses, with very
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53 1178 low RSD for major elements (<10 %, Table 4). Moreover, they all have a
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55 1179 similar composition in terms of major elements, except NTE02 that has a
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57 1180 lower content in most of them to compensate its MnO enrichment (> 4 wt
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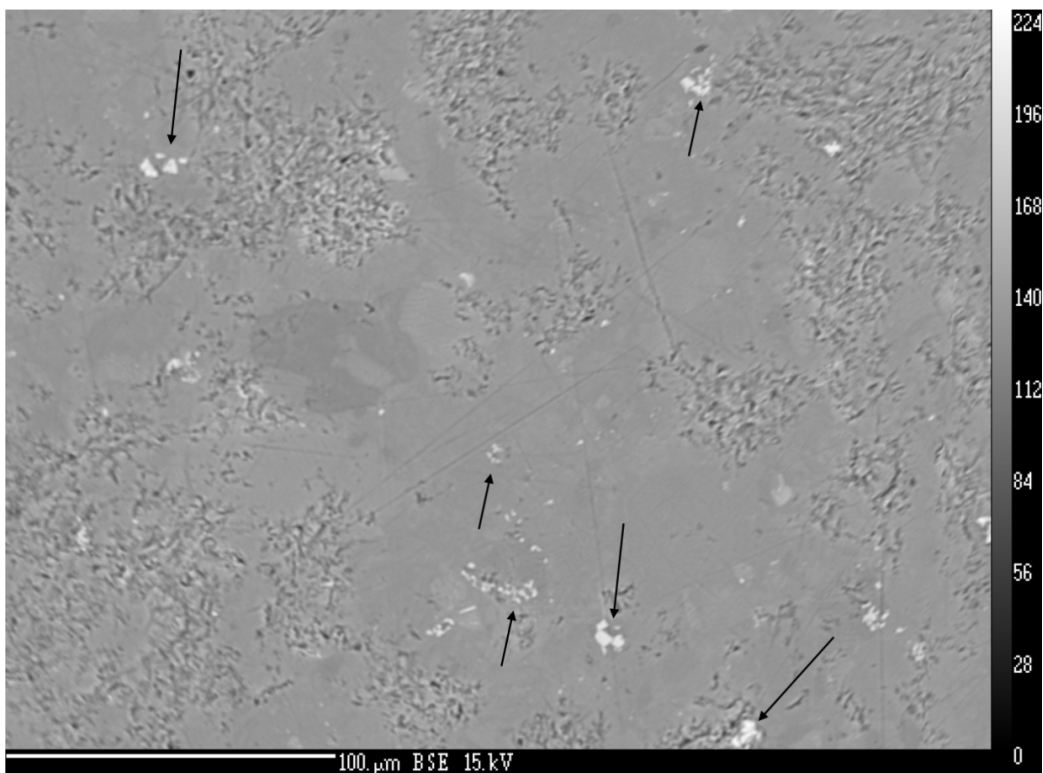


Figure 14: BSE image from the NTE04 flight model. Bright spots correspond to Cr oxides.

1181 %). In Figure 11, these targets are represented by circles. Even for their
1182 minor element concentrations, their RSDs are lower than 20 % except for a
1183 few exceptions, such as the Cr for NTE04 (light blue circle). In this target,
1184 there is 0.55 wt % of Cr_2O_3 , which is the highest amount of Cr in all the
1185 calibration targets. Cr is known to form chromites when its content is ele-
1186 vated [27], which can explain the elevated RSD at 73 % for the Cr content.
1187 Chromites are indeed observed in the BSE image (Figure 14), corresponding
1188 to the bright spots. Nevertheless, besides Cr, the RSDs obtained for the
1189 minor elements in these targets are mostly below 10 wt %, which make them
1190 very useful for the minor elements' calibration.

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10 1191 Minor and trace element's quantification is given in Table 5, for these
11 1192 particular targets along with all the others.
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15 1194 The shergottite target is a replicate from ChemCam Calibration targets
16 [27]. Besides the SPS process, it has been made from the same methodology
17 1195 as the minor-doped targets, and therefore is a glassy material, and very
18 1196 homogeneous. Both quantitative techniques give very comparable results.
19 1197 Observed differences are smaller than the RSDs of both techniques, as seen
20 1198 for the Si and Ca contents (1 wt% difference for the SiO₂ content, with RSDs
21 1199 between 2 and 4% and 1 wt% difference in the CaO content with 3% RSD
22 1200 for both techniques.
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31 1202 *6.4. Primary Igneous Minerals*

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33 1203 Quantitative analyses of these targets (Andesine, Diopside, Enstatite,
34 1204 Olivine, Ferrosilite) are presented in Table 4. The LA-ICP-MS compositions
35 1205 are similar to the EMPA results (squares in Figure 7-1). A few differences
36 1206 can still be observed, as these samples correspond to natural minerals and
37 1207 therefore a few impurities can still be present. Nevertheless, LA-ICP-MS
38 1208 measurements give generally smaller RSDs, as the analysis spot size is wider.

39 1209 Figure 15ab shows the quantitative values of these feldspars, pyroxenes
40 1210 and olivine in their respective ternary diagram, where the LA-ICP-MS val-
41 1211 ues are represented by squares and the EMPA values by circles. It can be
42 1212 observed that the composition (obtained from both techniques) falls into the
43 1213 appropriate field for each target. Olivine is calculated to be a Fo₆₄ from LA-
44 1214 ICP-MS and Fo₆₅ from EMPA, which is in concordance with the description
45 1215 of this natural target. One difference can be noted though, concerning the an-
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10 1216 desine: the Ca content is higher from the EMPA than from the LA-ICP-MS
11 1217 result (8.07 wt% vs 6.24 wt%, rep). To a lesser extent, the EMPA results for
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13 1218 the orthoclase target also show a slight enrichment in K₂O compared to the
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15 1219 LA-ICP-MS predictions (13.03 vs 12.23 wt%, resp.). This can be observed
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17 1220 as well in Table 4, and in Figure S1 in supplementary material. In both
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19 1221 cases, the EMPA technique gives Si and alkali contents closer to the theory.
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21 1222 Besides the fact that both techniques give appropriate results with a sum
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23 1223 of oxides around 100 wt%, it seems in this case that the EMPA technique
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25 1224 gives results more consistent with the expected stoichiometry. However, in
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27 1225 Figure 15c it can be noted that both techniques give a similar result in the
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29 1226 Al/Si vs (Fe+Mg)/Si plot. One reason to include mineral targets among the
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31 1227 SCCT was to enable creation this type of reference plot, in order to better
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33 1228 constrain our quantitative models for Martian igneous rocks. In that sense,
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35 1229 both techniques give consistent compositions and can be used for reference.

36 1230 In Figure 11, these mineral targets are represented by squares. It can be
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38 1231 observed that the RSD values for major elements (>1 wt%) are below 10%
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40 1232 relative error. Concerning the minor elements, some show a high RSD, such
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42 1233 as the diopside (orange square) with a RSD > 100 % for the Cr, Ni and Cu
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44 1234 elements (1461, 360 and 7.8 ppm, resp.), but most of the minor elements
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46 1235 have a RSD below 40 % for the Orthoclase (light green squares), with only
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48 1236 20 % RSD for Sr, present at 2.9 ppm. Rb, which substitutes easily with K,
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50 1237 is elevated (0.9 wt %) and has a low RSD (2.6 %). Also, for minor elements
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52 1238 are all < 25 % for the Enstatite target (red squares).

53 1239 In summary, these results show that these minerals are overall homoge-
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55 1240 neous with very few impurities.

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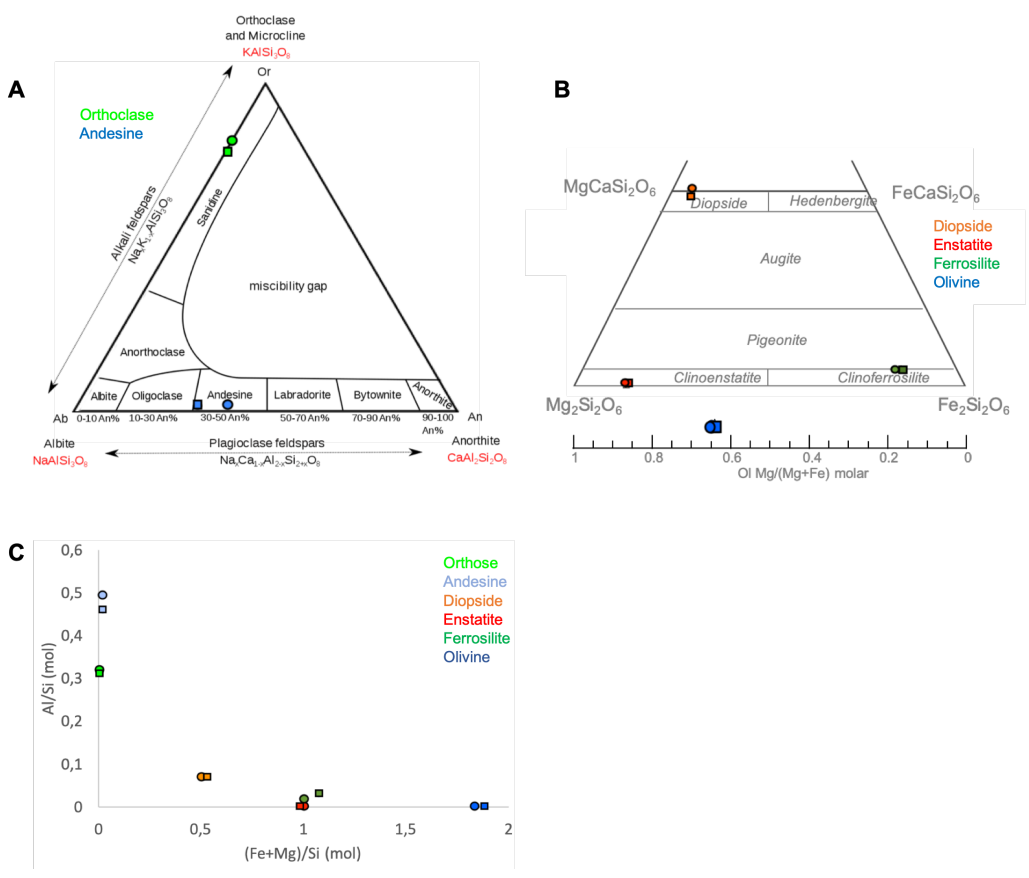


Figure 15: A. Ternary diagram for feldspars; B. Ternary diagram for pyroxenes and Mg number for olivines; C. Al/Si vs (Fe+Mg)/Si plot in molar ratios to show the reference compositions of these minerals. LA-ICP-MS values are represented by squares and EMPA values by circles.

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9 1241 *6.5. Synthetic targets*

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11 1242 The synthetic targets (TSRICH and Apatite) were not sampled with the
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13 1243 LA-ICP-MS technique. The Apatite being a phosphate, this would have re-
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15 1244 quired a different setup for the LA-ICP-MS method due to the important
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17 1245 isobaric interferences on mass ^{31}P . Moreover, as this target was designed
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19 1246 stoichiometrically, its composition was checked frequently using the EMPA
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21 1247 technique, which demonstrated a very homogeneous sample with RSDs < 12
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23 1248 % (Tables 4, 5, and Figure 11). Besides the calcium, it contains 41.65 wt%
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25 1249 P_2O_5 , with 2.98 wt% Cl, 1.82 wt% F, along with 0.016 wt% H. The apatite
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27 1250 chosen for the flight model (called "TAPAG") is represented in a ternary
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29 1251 diagram where the apatites found in meteorites are overplotted [101], as well
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31 1252 as apatites observed with ChemCam on MSL (blue area) [103] (Figure 16).

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33 1253
34 1254 The TSRICH target was not analysed by LA-ICP-MS technique either
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36 1255 (nor with EPMA), due to technical issues and the lack of reference for the
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38 1256 sulfur content. However, a good estimation of its composition can be made
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40 1257 from the known composition of its components, which are the BHVO-2 basalt
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42 1258 and a commercial K sulfate. Even though this target has been shown to be
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44 1259 relatively heterogeneous for most of its elements from LIBS and XRF analysis
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46 1260 [80], K and S are overall homogeneous in this sample, at least at the LIBS
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48 1261 scale (see part 5.1). Table 4 shows that it contains almost 40 wt% K_2O and
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50 1262 32 wt % SO_3 based on its theoretical content. Even though these contents
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52 1263 are only theoretical (not measured), they are nonetheless consistent with the
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54 1264 XRF observations [80].
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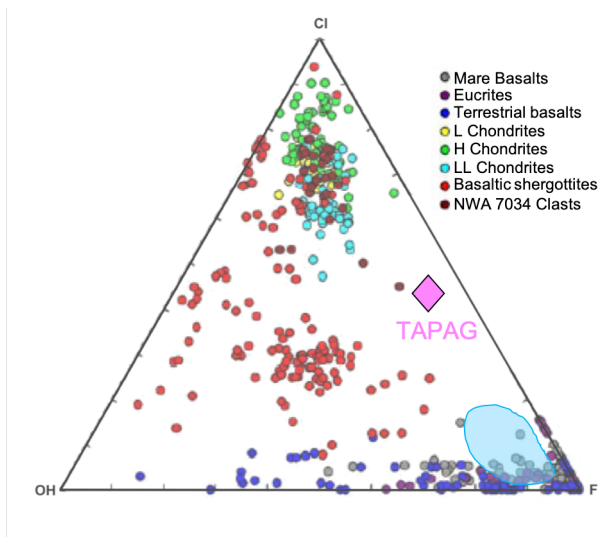


Figure 16: Cl, F, H ternary diagram modified from [101]. Apatites found on the Moon, terrestrial basalts and Mars meteorites are shown in circles [125, 126, 127, 128, 129, 130]. Apatites found by ChemCam at Gale crater are represented by the blue area [103]. The TAPAG sample, on-board the Perseverance rover, is represented by a pink diamond.

Type	Target_Name	Sr	RSD (%)	Li	RSD (%)	Rb	RSD (%)	Cr	RSD (%)	Ba	RSD (%)	Ni	RSD (%)	Cu	RSD (%)	Zn	RSD (%)	H (wt %)
Ankerite	LANKE0101	107.4	7.7	5.6	3.6	4.0	40.7	9.2	43.2	6.7	20.9	3.7	16.6	1.9	52.4	625.5	231.6	
BHVO2	LBHVO20406	410.7	7.2	6.7	6.8	15.3	10.5	342.4	40.2	192.6	8.9	134.0	13.7	162.1	11.6	147.2	7.0	
Calcite	LCA530106	232.9	7.0	0.2	24.8	0.1	112.6	13.0	159.9	2.3	10.6	0.6	24.2	0.6	42.8	4.9	19.2	
Chert	LCMB0006	2.4	24.2	1.6	22.2	6.1	32.3	2.7	25.8	6.8	25.0	8.9	24.6	4.8	30.1	30.4	24.0	
JMn1	LJMN10106	750.3	6.7	70.5	11.9	12.6	9.3	16.2	30.0	1814.2	12.0	14735.3	9.7	13470.8	10.4	1069.7	11.6	
JSC1	LJSC10304	1343.4	8.8	15.0	5.1	30.1	9.0	106.1	40.0	904.6	7.7	60.5	19.6	19.1	24.4	229.6	8.5	
Siderite	LSIDE0101	72.2	8.1	0.6	11.7	0.4	8.1	4.1	40.4	18.6	12.3	0.5	11.3	124.5	13.2	2687.9	35.6	
NTE01	NTE010301	67.8	2.3	42.5	6.7	72.7	9.7	626.9	48.7	80.9	1.9	490.8	14.0	1982.0	8.8	3582.7	3.3	
NTE02	NTE020106	231.4	6.2	89.6	4.8	3994.6	3.6	4359.9	16.9	523.2	2.7	901.2	2.4	276.1	3.2	783.3	3.4	
NTE03	NTE030106	97.3	2.5	55.6	3.3	269.7	13.0	1308.1	8.4	2090.1	2.6	1677.0	1.1	392.5	3.0	8608.6	3.3	
NTE04	NTE040106	1528.5	1.7	155.4	3.6	151.7	2.5	5523.4	73.1	1588.0	2.7	3316.2	8.0	107.2	4.2	1369.3	5.4	
NTE05	NTE050301	1057.4	2.0	10.6	4.3	5.7	7.8	1173.3	45.5	146.6	2.1	4827.5	3.2	65.5	4.4	2133.3	2.6	
Andesine	PMIAN0106	744.4	1.7	33.8	3.3	14.6	5.2	587.4	82.4	155.8	2.6	72.3	74.6	6.3	37.1	9.2	15.5	
Diopside	PMIDN0302	65.7	7.7	4.4	7.7	4.8	35.9	1461.0	217.0	53.4	34.5	360.3	230.1	7.9	151.6	31.1	11.2	
Enstatite	PMIEN0602	0.8	21.6	2.3	9.9	0.1	8.3	361.8	21.8	1.4	17.0	169.6	21.6	3.7	25.3	12.2	13.7	
Olivine	PMIFA0306	0.8	29.8	7.5	19.1	0.1	15.6	255.1	54.0	0.9	32.3	1512.9	20.0	682.5	90.4	616.4	20.9	
Ferrosillite	PMIFS0505	30.4	15.4	3.7	8.9	2.4	21.6	785.5	55.9	15.9	15.0	190.1	59.7	11.0	23.8	33.7	2.4	
Orthoclase	PMIOR0507	2.9	20.6	7.2	12.6	9054.6	2.6	205.0	33.7	30.7	7.4	48.1	45.8	3.3	14.0	4.5	15.1	
Shergottite	SHERG02	608.0	3.1	6.4	13.0	0.2	11.8	5.3	6.4	1189.7	5.1	370.9	1.6	11.2	21.3	6.8	8.7	
Serpentine	TSERP0102	0.2	30.4	0.1	23.7	0.2	137.5	980.9	17.4	0.3	33.6	1427.1	67.4	14.0	42.1	28.7	11.2	3.3
		P205 (%)	Cl (%)	F (%)														
Apatite	TAPAG0205	41.61	2.98	1.82														
		S03 (%)																
S-rich basalt	TSRICH0404	32.17																

Table 5: LA-ICP-MS/MS compositions for minor elements (in ppm except when % is mentioned) in all the LIBS SCCT targets (except for the apatite, compositions come from EMPA, and TSRICH target that is theoretical)

6.6. Comparison between Flight targets and Calibration Replicates

The set of calibration replicates (CR) discussed here is the one that was analysed with the FM/EQM setup in LANL, during the calibration campaign of SuperCam [3, 2]. These replicates were only quantified using EMPA. This set of CR and the flight targets are homogeneous and qualitatively they present similar compositions [80]. The flight targets can be used to validate the quantification models (developed using the CR calibration targets acquired in LANL) [15, 16].

Quantitative results from EMPA for these two sets of replicates are presented in Figure 17. The average content for each element is shown for both CR and FM replicates, along with their RSDs as error bars. The compositions deduced from EMPA on the CR and the FM replicates are in excellent agreement. A few differences are only observed for Si, Fe and Ca, but the

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9 1279 RSDs always overlap between the two replicates. The main difference is for
10 1280 the SiO₂ in the Chert sample, with relatively low RSDs that overlap only par-
11 1281 tially. However, the shift observed in SiO₂ content is lower than the RMSE
12 1282 observed on ChemCam (which is around 11 wt % for this SiO₂ content -
13 1283 [30]). Therefore, there are no differences in quantitative values between the
14 1284 two sets of replicates (LANL calibration and flight) that could impact the
15 1285 accuracy of the modeling.

1286 6.7. Summary

1287 The distribution of the major and minor element concentrations (Figure
1288 18) covers a wide range of contents, and often larger than those observed on
1289 Mars with ChemCam up to sol 2500. The iron content in the SCCT is not as
1290 elevated as seen on Mars, but the values higher than 50 wt % at Gale crater
1291 correspond either to iron meteorites [131] or to iron oxide-rich diagenetic fea-
1292 tures [132, 133]. Some gaps in the range can still be observed, for example
1293 the SiO₂ content, with no target between 70 wt% and 95 wt%. Such high
1294 SiO₂ is not uncommon in nature, but will be covered by the wide terrestrial
1295 database [30]. Ca, K and Mn each have a single high value well above the
1296 other standards, and the terrestrial database will fill the gaps. These calibra-
1297 tion targets cover a wide range, from a mafic to felsic silicate composition,
1298 to a carbonate or a phosphate-type of sample. Extreme compositions such
1299 as pure Fe or Mn oxides will be covered by the terrestrial database, as well
1300 as phyllosilicates or pure sulfates samples.

1301 Minor and trace elements from the SCCT also show a wide range of distribu-
1302 tions (more details can also be found in supplementary material, Figure S2).
1303 Compared to the terrestrial database, Li, Rb and Cu go beyond its range

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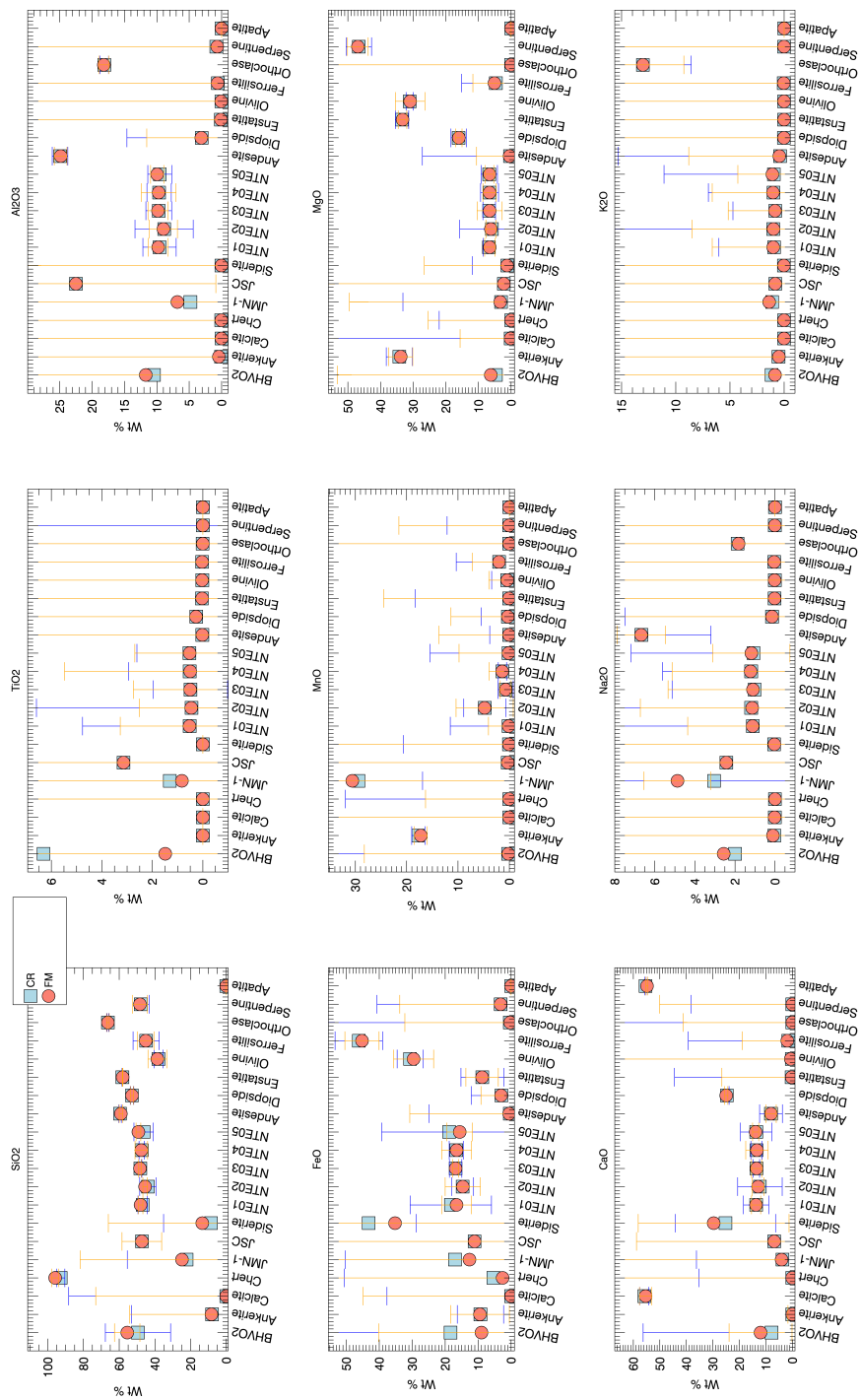


Figure 17: Average values from EPMA technique for the FM (orange) and CU (blue) replicates of the SCCTs. Error bars represent the RSDs obtained from EMPA. The RMSE obtained from ChemCam LIBS quantitative model can be found in [30].

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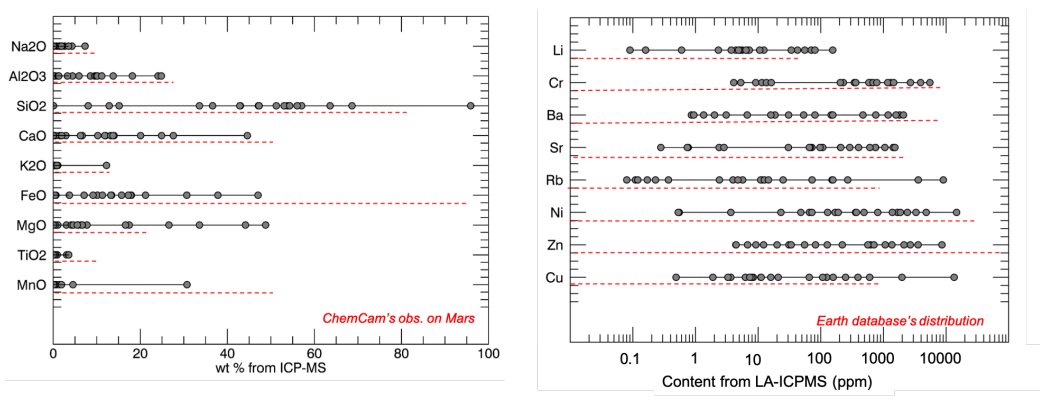


Figure 18: Quantitative compositional range of the SCCTs onboard Perseverance, for major and minor elements. The TSRICH target is not included here, as its composition is theoretical only. Dashed red line represents the range observed at Gale crater from ChemCam for the major elements (left), and the distribution of minor elements from SuperCam’s Earth database on the right.

1304 and therefore will be of great help if uncommonly high values are observed
1305 on Mars. Compared to ChemCam’s observations at Gale crater for Ba, Rb,
1306 Sr and Li (minor elements that are quantified), the SCCT are covering their
1307 distribution well (Figure S2 for details). Moreover, these calibration targets
1308 are covering a sufficient range in terms of minor element to build calibration
1309 curves. This is not discussed in this study but can be found in supplement-
1310 ary material as well, part 5, Figure S3. Finally, these on-board calibration
1311 targets are nearly identical in terms of composition to the replicate calibra-
1312 tion targets. They are of great importance to verify the quantitative models
1313 performed on Earth.

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9 1314 **7. Use of the SCCT on Mars**

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11 1315 Concerning the LIBS technique, calibration activities must fit within the
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13 1316 overall operational scenario. One of the restrictions encountered for the oper-
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15 1317 ational activities is sequence duration, which needs to be kept relatively short
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17 1318 in order to accommodate all of the high-priority science and engineering ac-
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19 1319 tivities on the rover. In order to avoid any activity longer than 30 minutes,
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21 1320 we have developed four different activities. Each activity will perform one
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23 1321 point analysis on 5 to 8 different SCCTs. Each point analysis uses only 10
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25 1322 shots, even though usually 30 shots per point are performed on martian tar-
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27 1323 gets. This is because of the proximity of the calibration targets to an optical
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29 1324 keep-out zone with the instrument [2, 9]. Mast movement is more efficient
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31 1325 when raster sequences proceed from bottom to top, and also from right to
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33 1326 left. With these constraints, each calibration activity has been strategically
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35 1327 planned in order to sample a wide variety of compositions each time. Each
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37 1328 activity consists of 1 RMI observation and 1 point of 10 shots on each of the
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39 1329 targets included in each series, as described below.

40 1330 Series 1 comprises 8 targets: Shergottite (ChemCam replicate), NTE05,
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42 1331 Siderite, Ankerite, serpentine, enstatite, andesine and the TSRICH. As the
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44 1332 choice of parameters on Mars will be done using only the brightest and dark-
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46 1333 est targets in terms of LIBS spectral signature (TSRICH for the brightest,
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48 1334 Chert for the darkest), this combination will allow a check for saturation of
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50 1335 the spectra, as the second most bright (andesine) as well as the second lowest
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52 1336 one (shergottite) are included. This combination also allows a wide range of
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54 1337 compositions, from mafic igneous minerals and overall basaltic composition
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56 1338 more or less altered, to the andesine plagioclase, with carbonates and the

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9 1339 S-rich target.

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11 1340 Series 2 contains 7 targets: NTE04, NTE03, JSC-1, BHVO-2, olivine,
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13 1341 diopside, and orthoclase. This series mainly contains mafic compositions
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15 1342 (NTE04, NTE03, JSC-1, BHVO-2, olivine, diopside), including olivine and
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17 1343 Ca-rich pyroxene diopside, but also includes the K feldspar, orthoclase.

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19 1344 Series 3 also contains 7 targets: NTE02, NTE01, JMn-1, Apatite, Fer-
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21 1345 rosilite, Calcite and Chert. This series has probably the widest range in
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23 1346 terms of rock type, with a phosphate, a carbonate and diverse silicates such
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25 1347 as the Chert (Si-rich) and the ferrosilite (Fe-rich orthopyroxene).

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27 1348 These three series constitute recurrent activities, with the aim of sam-
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29 1349 pling all of the calibration targets every two months at the beginning of the
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31 1350 mission. These data will be of prime importance in order to validate different
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33 1351 aspects, like the Earth-Mars differences and the quantification models, which
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35 1352 are developed using data acquired from laboratory measurements. Also, the
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37 1353 recurrence of the activity gives a good opportunity to evaluate the dust de-
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39 1354 position on these targets with time. Since landing, these series have been run
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41 1355 two times and data are being analysed in details. The Titanium target is not
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43 1356 part of these series, but represents a dedicated activity for the wavelength
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45 1357 correction. This will be a recurrent activity that will be run monthly, and
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47 1358 more often at the beginning of the mission.

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51 1360 For the Raman technique, two activities were built using the dedicated-
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53 1361 Raman targets - the diamond and the ertalyte [9]. One activity focuses on
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55 1362 the Raman "health check", looking at the diamond, whereas the other one
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57 1363 is dedicated to the ertalyte observation in order to understand and better

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9 1364 interpret the detection of organics on Mars, but also to check the ageing of
10 1365 such a component under Mars UV radiations. More details about the science
11 1366 objective of these Raman targets can be found in [9]. The diamond observa-
12 1367 tion will be performed every month, whereas the ertalyte's observation will
13 1368 be done every three months or less, depending on science requests. Through
14 1369 sol 135 of the mission, the diamond and the ertalyte targets were analysed
15 1370 twice.

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22 1371 Two series are dedicated to the Raman fingerprints of the geological tar-
23 1372 gets. As seen in part 5.3, not all the targets have a detectable signal us-
24 1373 ing Raman spectroscopy. Therefore, one series contains the apatite, calcite,
25 1374 TSRICH and the white paint, which are the geological targets showing the
26 1375 best Raman signal. The second series contains targets that have shown some
27 1376 signal from lab measurements, but to a smaller extent: the enstatite and
28 1377 olivine. The first series will be obtained every year, whereas the second
29 1378 series' cadence will depend on the signal obtained.

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37 1379 For the VISIR technique, the SCCT White target is to be used frequently
38 1380 for calibration of radiance spectra to relative reflectance and to track in-
39 1381 strument performance and monitor its behaviour with the always evolving
40 1382 environmental conditions. The Black target assists with confirming instru-
41 1383 ment fields-of-view, whereas the white paint on the calibration target housing
42 1384 (target 34) is used to assist with wavelength calibration.

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49 1385 A selection of the SCCT targets shown in Figure 2 will be monitored
50 1386 throughout the mission to determine instrument stability and for comparison
51 1387 to observations of martian materials. The meteorite (target 36) can be viewed
52 1388 for comparison to mafic-rich materials, although no laboratory VISIR spectra

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1389 exist for this target. Care is taken to avoid the darkened LIBS laser spots
1390 on the LIBS targets.

1391 Some of the SCCT have been analysed on Mars with the VISIR techniques
1392 (see part 5.2), at several times of day, in order to have different illumination
1393 and instrument temperature conditions.

1394 8. Conclusions

1395 On-board the *Perseverance* rover, the SuperCam instrument is being used
1396 as a remote-sensing facility to analyze the surface at Jezero crater using a
1397 suite of five coaligned techniques: the LIBS technique to determine the ele-
1398 mentary composition of the targets, Raman and VISIR spectroscopy for the
1399 mineralogy and structural information, a microphone to give access to some
1400 physical parameters of the sampled rocks along with atmospheric science,
1401 and a color remote micro imager to give the context of the analyses. Super-
1402 cam requires constant monitoring of the signal acquired from each technique,
1403 and this is why a set of 36 calibration targets have been developed. A dedi-
1404 cated set of 22 geological samples mimic the martian composition previously
1405 observed in Gale crater but also at Jezero from orbit. These targets were de-
1406 rived from igneous minerals, standards, natural rocks, basaltic glasses doped
1407 with minor elements and synthesised targets. A Titanium plate, a former
1408 ChemCam shergottite target and a martian meteorite thin section are also
1409 on-board as calibration support. Thus, all of the target compositions cover
1410 a wide range of major (Si, Ti, Al, Fe, Mg, Ca, Na and K) and minor ele-
1411 ments' (Ba, Sr, Li, Zn, Mn, Ni, Cr, Cu, Rb) contents. These targets can
1412 be specifically dedicated to LIBS analysis or/and to non-destructive anal-

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9 1413 ysis for mineralogical studies. Replicates as well as the flight unit targets
10 1414 have been heavily analysed by various analytical techniques (LA-ICP-MS,
11 1415 EMPA, XRF, LIBS, Raman, VISIR) to check their compositional homo-
12 1416 geneity. These analyses demonstrate that these geological calibration targets
13 1417 display a very homogeneous composition between the replicates and within
14 1418 each specimen, even for the trace elements. This allows the use of the flight
15 1419 unit targets for the establishment of future *in situ* calibration curves, and for
16 1420 validation of quantitative models. Considering that the thousands of analyses
17 1421 performed by ChemCam since 2012 allowed multiple discoveries and insight
18 1422 on Mars geological history, SuperCam will be able to provide essential clues
19 1423 about Jezero’s geological settings in order to better choose the samples to
20 1424 drill and for eventual return to Earth on Mars Sample Return.

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