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1 Post-Landing Major Element Quantification Using 2 SuperCam Laser Induced Breakdown Spectroscopy

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 50

51 **Abstract**

52 The SuperCam instrument on the *Perseverance* Mars 2020 rover uses a pulsed 1064 nm laser
 53 to ablate targets at a distance and conduct laser induced breakdown spectroscopy (LIBS) by
 54 analyzing the light from the resulting plasma. SuperCam LIBS spectra are preprocessed to
 55 remove ambient light, noise, and the continuum signal present in LIBS observations. Prior to
 56 quantification, spectra are masked to remove noisier spectrometer regions and spectra are
 57 normalized to minimize signal fluctuations and effects of target distance. In some cases, the
 58 spectra are also standardized or binned prior to quantification. To determine quantitative
 59 elemental compositions of diverse geologic materials at Jezero crater, Mars, we use a suite of
 60 1198 laboratory spectra of 334 well-characterized reference samples. The samples were
 61 selected to span a wide range of compositions and include typical silicate rocks, pure minerals
 62 (e.g., silicates, sulfates, carbonates, oxides), more unusual compositions (e.g., Mn ore and
 63 sodalite), and replicates of the sintered SuperCam calibration targets (SCCTs) onboard the
 64 rover. For each major element (SiO₂, TiO₂, Al₂O₃, FeO_T, MgO, CaO, Na₂O, K₂O), the database
 65 was subdivided into five “folds” with similar distributions of the element of interest. One fold was
 66 held out as an independent test set, and the remaining four folds were used to optimize
 67 multivariate regression models relating the spectrum to the composition. We considered a
 68 variety of models, and selected several for further investigation for each element, based
 69 primarily on the root mean squared error of prediction (RMSEP) on the test set, when analyzed
 70 at 3 m. In cases with several models of comparable performance at 3 m, we incorporated the
 71 SCCT performance at different distances to choose the preferred model. Shortly after landing
 72 on Mars and collecting initial spectra of geologic targets, we selected one model per element.
 73 Subsequently, with additional data from geologic targets, some models were revised to ensure
 74 results that are more consistent with geochemical constraints. The calibration discussed here is
 75 a snapshot of an ongoing effort to deliver the most accurate chemical compositions with
 76 SuperCam LIBS.

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122

123 1. Introduction

124 The SuperCam instrument suite on the Mars 2020 rover Perseverance [1] includes the second
 125 remote laser-induced breakdown spectroscopy (LIBS) instrument to operate on another planet.
 126 In addition to LIBS, SuperCam capabilities include visible and infrared reflectance spectroscopy,
 127 time-resolved Raman and luminescence spectroscopy, remote imaging, and acoustic recording
 128 [2,3]. SuperCam’s first use was followed closely by the MarSCoDe instrument suite on the
 129 Zhurong rover, which consists of a LIBS instrument, an infrared spectrometer, and an imager
 130 [4]. Both instrument suites have LIBS instruments patterned after ChemCam [5,6], which has
 131 been used on Mars since 2012 as part of the payload of the Mars Science Laboratory rover
 132 *Curiosity*.

133 SuperCam contributes to three Mars 2020 mission science goals: to study the geology and
 134 geochemistry of Jezero crater; to investigate habitability, materials with biosignature
 135 preservation potential, and evidence of past life; and to assemble a cache of returnable
 136 samples, including searching for the best samples and documenting their geological context and
 137 general character [1]. The SuperCam investigation’s specific goals include rock identification;
 138 characterization of sedimentary stratigraphy and alteration, morphology, and texture; the search
 139 for organic molecules and biosignatures; characterization of volatile elements; and investigation
 140 of surface varnishes and coatings, regolith, igneous history, and atmospheric properties. LIBS
 141 contributes to all of these goals as described in [2].

142 SuperCam’s instrument architecture is similar to ChemCam’s but with notable changes to
 143 facilitate SuperCam’s additional functionality. Both instruments consist of an internal body unit
 144 containing the spectrometers and an external mast unit with the laser and 110 mm aperture
 145 telescope to acquire observations of targets around the rover. SuperCam’s telescope is
 146 improved compared to ChemCam, enabling a slightly smaller laser footprint on targets with its
 147 ~12 mJ, 1064 nm, 3-4 ns long laser pulse [2]. Plasma light is transmitted from the telescope to
 148 the spectrometers in the body of the rover via a ~6 m optical fiber and an optical demultiplexer
 149 [3]. Both ChemCam and SuperCam use a trio of spectrometers to cover wavelengths between
 150 ~240 and 850 nm at similar wavelength resolution. The ultraviolet (UV) and violet (VIO) spectral
 151 ranges on both SuperCam and ChemCam are covered by nearly identical Czerny-Turner [7]

152 spectrometers and ungated detectors. Unlike ChemCam, which uses a third Czerny-Turner
 153 spectrometer, SuperCam uses a transmission spectrometer with a gated intensifier to cover the
 154 ~535-850 nm range. This spectrometer enables remote time-resolved Raman spectroscopy.
 155 This spectrometer has similar resolution to ChemCam over much of that range but has a factor
 156 of 2 better resolution in the Raman range from 535 to ~610 nm. In addition to superior
 157 resolution, the transmission spectrometer affords other advantages, including reduced collection
 158 of ambient light (sunlight) due to a shorter exposure (10 μ s is used for LIBS). The disadvantage
 159 of the intensifier is increased noise relative to ChemCam's bare CCD (charge-coupled device).
 160 The transmission spectrometer transmits light into three spectral ranges (Green, Orange, and
 161 Red), thus using nearly three times the number of spectral channels relative to ChemCam
 162 (Table 1), which uses ~2000 channels over a larger spectral range. SuperCam cannot acquire
 163 simultaneous LIBS and Raman spectra even though both use the same spectrometer, because
 164 the laser is frequency doubled and its beam path is changed for the Raman observations. Table
 165 1 summarizes the SuperCam spectrometer spectral ranges and number of spectral channels in
 166 a typical LIBS Calibrated Data Record (CDR) product. These values are valid for both Mars
 167 spectra and the laboratory spectra used here.

Table 1: Overview of SuperCam LIBS calibrated data record (CDR)

Spectrometer	Abbreviation	Wavelength range (nm)	# of spectral channels after stitching	Range of channel indices used in stitching
Ultraviolet	UV	243.79 - 341.36	2040	n/a
Violet	VIO	379.26 - 464.54	2037	n/a
Green	VNIR	537.57 - 619.82	1237	600-1837
Orange		620.08 - 712.14	1114	471-1587
Red		712.17 - 852.77	1505	345-1850

168
 169 A key advantage of SuperCam's LIBS system is the inclusion of a much larger number of
 170 onboard calibration targets that cover a greater compositional range than ChemCam's. The 23
 171 LIBS targets include pure igneous mineral compositions, basaltic targets doped with trace
 172 elements, and a number of targets simulating typical rock compositions [8,9]. A titanium plate is
 173 included for wavelength calibration as was done on ChemCam. These onboard targets are not
 174 adequate to train a regression model, but they provide ground-truth comparisons that can be
 175 used to evaluate calibration models under martian conditions.

176
 177 The *Perseverance* landing site, Jezero crater, appears to differ substantially in rock type and
 178 composition from Curiosity's landing site in Gale crater. Like Gale crater (e.g., [10–12]), Jezero
 179 crater was once a large lake, as indicated by a notable deltaic formation and outflow channel

180 which demonstrates that the crater was filled with water (e.g., [13–15]). However, the local
181 chemistries appear to be different. The Curiosity rover has encountered three main stratigraphic
182 groups in Gale crater: the Bradbury group, the Mount Sharp group, and the Siccac Point group
183 [10]. The Bradbury group consists of sorted detrital plagioclase-phyric basaltic sedimentary
184 rocks transported from the crater rim [16,17]. The composition of the Stimson formation in the
185 Siccac Point group is similar to the Mars global dust composition, and it consists of lithified
186 aeolian dunes [16]. The Murray formation, which constitutes much of the Mount Sharp group is
187 a dominantly lacustrine formation that has a relatively consistent silica-rich subalkaline basalt
188 composition that is distinct from the Bradbury group: with a more silica-rich basaltic source rich
189 in plagioclase and Fe, low in Ca and Mg (e.g., [18]). By contrast, from orbit, Jezero crater's
190 upstream regions contain olivine and pyroxene, areas of Jezero crater just inside the rim have a
191 distinctive Mg carbonate signature, and the crater floor farther from the rim appears to have an
192 olivine-rich mafic unit (e.g., [19]). The team thus expects minerals rich in Mg such as olivine
193 and its alteration-pathway minerals, e.g., serpentine and talc [20] as well as Mg-rich clays, and
194 C (carbonates; e.g. [21–23]). To address these expectations, we tuned both the onboard targets
195 and the overall spectral library with more carbonates and Mg-rich compositions.

196 1.1. Overview

197 This paper provides an overview of the current state of the SuperCam team's ongoing efforts at
198 developing quantitative calibration models for the major element oxides (SiO_2 , TiO_2 , Al_2O_3 ,
199 FeO_T , MgO , CaO , Na_2O , K_2O), and possible next steps. We first discuss the challenges of
200 quantitative LIBS and the different approaches to calibration. This is followed by a description of
201 the laboratory setup and details regarding the collection of a diverse database of LIBS spectra
202 used to train and test the calibration models. We then discuss the preprocessing steps applied
203 to the spectra, followed by the organization of spectra into training and test sets and the
204 assessment of data quality and removal of outliers. We discuss the multiple regression
205 algorithms tested and how models were tuned and selected for optimal performance. Finally, we
206 discuss the results of applying the selected models to data on Mars and potential next steps in
207 our effort to improve the accuracy of SuperCam LIBS quantification.

208 1.2. The Challenges of Quantitative LIBS

209 Deriving quantitative elemental abundances of geologic targets from LIBS spectra is
210 challenging, both because of the nature of the stand-off LIBS technique itself and the nature of
211 the targets being analyzed. The distance to the target and target properties influence the
212 recorded LIBS spectra. The laser spot size, and therefore the laser irradiance on the target,
213 varies with distance: the spot size is $\sim 170 \mu\text{m}$ at 2.4 m and increases to $\sim 370 \mu\text{m}$ at 5.5 m [15].
214 The amount of energy absorbed by a target per laser pulse is also strongly dependent on the
215 target opacity and albedo at the laser wavelength. Some materials absorb the laser well, but
216 others, particularly those with large crystals that are transparent or translucent to the laser, may
217 be absorbed poorly or not at all (e.g. [23,24]) resulting in low signal to noise or a lack of any
218 discernible LIBS signal. Moreover, the laser spot size is often bigger than the individual crystals
219 or grains in the geologic sample which can lead to heterogeneous mixtures in the targets
220 probed.

221 An additional challenge is that LIBS spectra record a process that is inherently transient: the
222 laser-induced plasma evolves rapidly during and after the laser pulse, changing in temperature,
223 density, and opacity [26]. Furthermore, the ions, atoms, and molecules in the plasma interact
224 with each other, causing the intensity of emission lines from any given element to depend on the
225 presence and concentration of other elements. Unconsolidated materials such as regolith/soil or
226 dust present an additional challenge; although they may absorb the laser well, the shock wave
227 from the laser ablation alter the material surface for subsequent laser shots and create a pit that
228 confines the plasma and changes its properties compared to an unconfined plasma generated
229 on a hard surface (the conditions under which our spectral database was acquired). Collectively
230 the chemical and physical effects that can complicate the simple relationship between emission
231 line strength and elemental abundance are called “matrix effects” [27].

232 For terrestrial LIBS applications, it is possible to mitigate these analytical challenges by, e.g.,
233 sample preprocessing, control of observation repeatability, and possibly by selection of
234 calibration samples that are matrix matched to specific targets of interest. For SuperCam and
235 other planetary LIBS instruments, these strategies are not available, but key features of LIBS
236 (e.g., speed, remote compositional analysis, and no sample-preparation requirements) led to
237 SuperCam’s selection as part of the rover payload.

238 Even when the laser is absorbed well and a quality LIBS spectrum is collected, quantifying the
239 compositions of rocks and minerals is challenging compared to LIBS applications in industrial
240 settings, where the range of compositions is relatively well constrained and the materials
241 themselves are homogeneous in terms of their physical properties and composition. Although
242 most Mars rocks are composed primarily of silicates and have a roughly basaltic composition
243 (e.g., [27–29]), experience from Gale crater with ChemCam shows that “extreme” compositions
244 (often pure minerals) are observed and are scientifically interesting targets (e.g. [31–33]). An
245 ideal quantification for Mars targets should be accurate for “typical” basaltic rocks, for pure
246 silicate minerals such as olivine and plagioclase, and also for “unusual” non-silicate
247 compositions such as manganese-, iron-, and titanium-oxides, sulfates, and carbonates.

248 Considering the range of variations in observational parameters and the expected heterogeneity
249 of samples expected at Jezero crater, a physics-based approach like “calibration-free LIBS”
250 (CF-LIBS; e.g., [34]) might seem attractive. However, the SuperCam instrument is not suitable
251 for CF-LIBS because the whole plasma evolution from initiation to extinction is recorded in each
252 spectrum, rather than only acquiring the spectrum during a narrow time-gate of the plasma
253 evolution. Furthermore, not all contributing components in martian targets are easily quantified
254 by LIBS (e.g., sulfur, or carbonates in a CO₂-dominated atmosphere), making the self-
255 normalization implied in CF-LIBS problematic [35]. For these reasons, we have not investigated
256 the use of CF-LIBS for the quantitative calibration model for SuperCam.

257 1.3. Multivariate vs Univariate Calibration

258 Our calibration approach was to seek an empirical calibration trained on data collected in the
259 laboratory. Empirical calibrations can be “univariate” or “multivariate.” Univariate calibration
260 relates a single variable such as intensity at a given wavelength, or the integrated intensity of a

261 fitted emission line, to the abundance of the element of interest. Multivariate models instead
262 incorporate information from many emission lines, and potentially from the entire spectrum, to
263 predict elemental abundances.

264 Univariate models have the advantage of being simple and easy to interpret, and the user has
265 complete control over which emission line is used. However, although univariate models can be
266 effective for minor and trace elements with few weak emission lines (e.g., [31,36]), they tend not
267 to perform as well as multivariate models for major elements [37]. Multivariate models can
268 incorporate information from the entire spectrum, including emission from elements other than
269 the element being predicted, to mitigate matrix effects outlined above.

270 Both univariate and multivariate models run the risk of giving spurious predictions for new data,
271 either due to the prediction model being overfitted (i.e. tuning the parameters such that the
272 model performs well on the training set but does not handle novel data well) or because the new
273 observation represents an unusual composition relative to the samples on which the model was
274 trained. If trained on a large and representative data set, the multivariate models have superior
275 performance [37,38]; we therefore chose to focus our efforts on the multivariate approach for
276 the major element calibrations discussed in this paper.

277 **2. Experimental**

278 **2.1. Setup**

279 The multivariate models used to extract quantitative chemical compositions are developed from
280 a spectral library of pressed rock powder and synthetic standards with known chemical
281 compositions. This spectral library was acquired prior to delivery of the SuperCam instrument to
282 the rover for assembly and integration. Data acquisition was performed in Los Alamos National
283 Laboratory using the flight Body Unit (i.e. the unit now in the *Perseverance* rover on Mars)
284 containing the spectrometers, and an Engineering Qualification Model (EQM) of the Mast Unit
285 (MU) containing the laser and telescope [2,3]. Differences between the EQM and flight versions
286 of the MU are minor. The most significant is that the flight MU uses an aluminum primary mirror
287 surface, while the EQM uses a nickel-coated aluminum mirror similar to ChemCam's [5]. The
288 flight mirror is an all-aluminum mirror because it was determined after the EQM build that the
289 nickel coating resulted in a slight degradation of the shape of the mirror at its normal
290 temperature on Mars (where it is maintained at $\sim -35^{\circ}\text{C}$) relative to the optimum shape at room
291 temperature on Earth. The change in mirror surfaces resulted in a noticeable improvement in
292 the resolution of the Remote Micro-Imager (RMI) images at Mars temperatures, but the change
293 in laser beam size was not noticeable; however, it may have had a small but unquantified effect
294 on the LIBS. The other effect of the all-Al mirror surface was a slight loss ($\sim 10\%$) in reflectivity in
295 the UV range. Both flight and test setups were corrected for their respective optical responses,
296 compensating for this and any other differences in optical response.

297

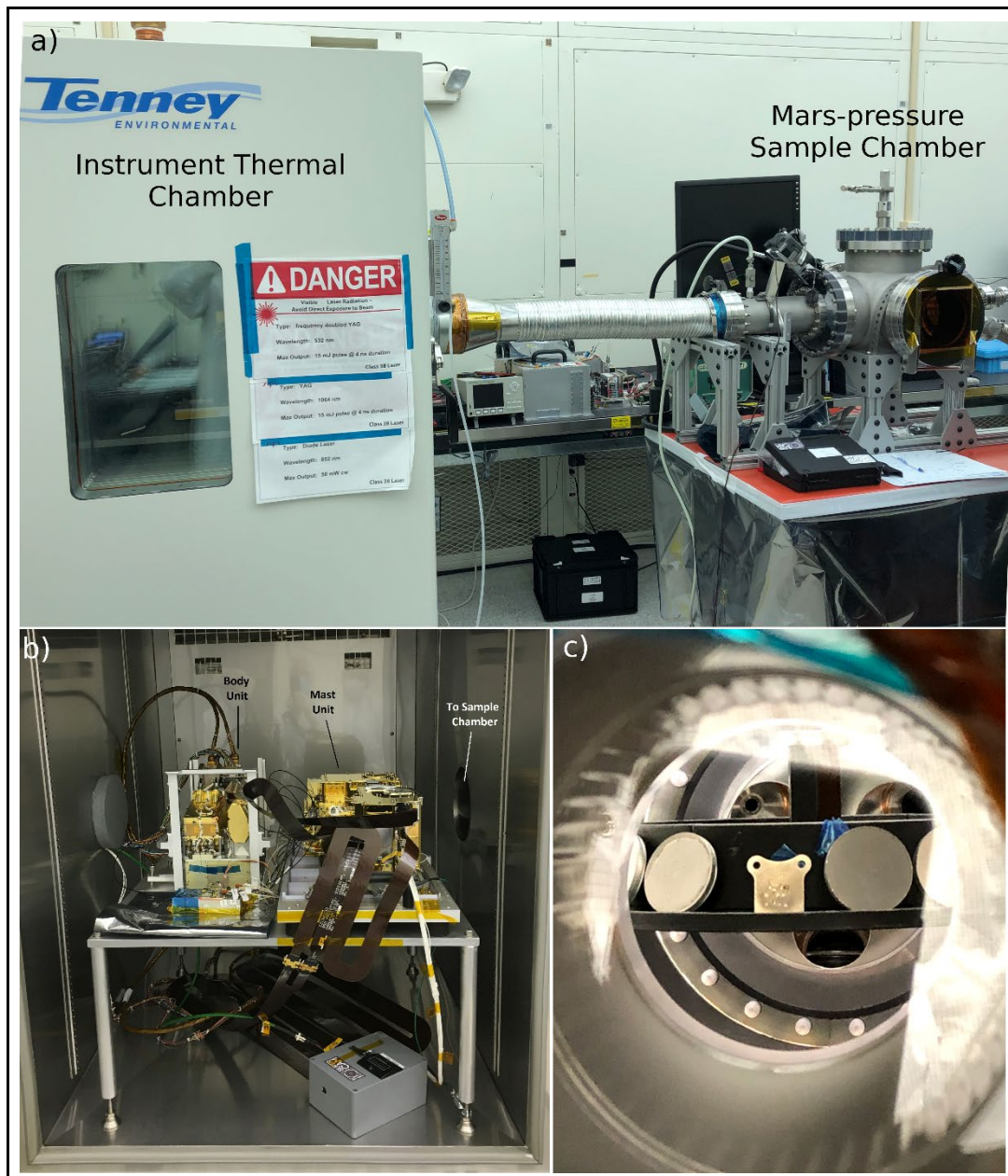


Figure 1: Photographs of the laboratory setup: (a) environmental chamber, with a tube connecting to the chamber containing standards to be analyzed; (b) SuperCam inside the environmental chamber and (c) view down the connecting tube of several pressed powder samples and a Ti plate ready for analysis. Photo credit: R. Wiens.

298 The experimental arrangement is shown in Figure 1. Because the SuperCam laser is designed
 299 to give optimum performance at “Mars-like” temperatures in the -30 to +10°C range, the
 300 instrument was maintained in a thermal chamber for laboratory measurements. The Body Unit
 301 was in the chamber too, since the detectors should be operated at temperatures below 0°C. It
 302 was observed during early testing that the compressor of the thermal chamber vibrated the
 303 instrument slightly, causing the laser beam position on the target to vary by up to ~500 μm at

304 nominal target distances. To provide consistent pointing such that successive pulses hit the
305 same location, the thermal chamber was cooled to -15°C and turned off while observations were
306 made of two targets, at which point the chamber was re-cooled to -15°C before repeating with
307 the next two targets. The chamber temperature never exceeded -7°C

308 Samples were placed in the Mars chamber (Figure 1), which accommodated ~ 16 pressed
309 pellets (30 mm diameter) plus a Ti plate control sample. The chamber was sealed and
310 evacuated to <100 mTorr (~ 10 Pa) pressure. Gas was introduced to bring the pressure to 5.5
311 Torr (733 Pa, the mean surface pressure at Jezero crater) using CO_2 , maintaining that pressure
312 with dynamic pumping so that the gas in the chamber was constantly refreshed. This minimizes
313 moisture and removes volatiles produced during ablation to minimize contamination of the
314 chamber window. Pressure was read by a vacuum gauge, which is calibrated for terrestrial air
315 composition (80% N_2). Pressure curves for CO_2 indicate that a reading of 3.5 Torr corresponds
316 to an actual pressure of 5.5 Torr. The pressure was maintained within $\pm 3\%$. Relative humidity in
317 the room was low ($\sim 20\%$); however, the pressed powder standards were stored without
318 desiccants, and notable hydrogen peaks in otherwise anhydrous standards suggest that the
319 pressed powders contained some adsorbed and/or absorbed water.

320 To be consistent with SuperCam optical geometry and to avoid unnecessary optical aberrations,
321 we used only a single window between the instrument and the samples, similar to the remote
322 warm electronics box (RWEB) window on the rover. To achieve this configuration while keeping
323 the targets at Mars pressure and keeping the instrument at Mars-like temperatures, a tube was
324 installed to enclose the beam path between the thermal chamber and the sample chamber. The
325 tube kept warm, humid air from entering the thermal chamber near the aperture of the
326 instrument, which would have resulted in condensation there. The tube extended to the window
327 of the sample chamber at Mars pressure (Figure 1). Different lengths of tubing were available,
328 so that targets could be observed at different distances.

329 Focusing was performed manually by setting the focus stage to the approximate distance to the
330 target, firing the laser, and checking the signal strength. Small adjustments to the focus were
331 made in the forward and backward directions to find the strongest signal. The focus was kept at
332 this position over a period of several days during the measurement campaigns, checking the
333 strength of the signal from a control sample (titanium plate) to ensure that focus was maintained
334 from one day to the next. The LIBS campaign was interrupted before the last standards were
335 observed, and upon resumption, a distance of 3.0 m was used instead of the original 2.85 m,
336 and a relatively small number of standards were observed at this slightly longer distance. In the
337 analyses discussed here, the data at 2.85 and 3.0 m are grouped together and referred to as
338 the "3 meter" data set.

339 2.2. Data for the spectral library were collected between 9 and 21 April
340 2019. Three separate locations were analyzed on each standard,
341 collecting 30 active and 30 non-laser (“dark”) spectra from each location.
342 The average spectrum for each location was calculated, excluding the first
343 five points to minimize surface contamination (e.g. adsorbed water). In a
344 few cases, four locations were probed if there was any question of the
345 validity of the first three observations. The laser was energized with a
346 current of 140 A, which yields 12 mJ of energy measured on target at
347 Mars-like temperatures after passing through the telescopic system and
348 the window between the thermal chamber and the sample chamber. For
349 the UV and VIO spectral ranges, signal was collected over 200 rows of the
350 detectors with an integration time set to 34 μ s, although without a shutter,
351 the effective integration time was much longer due to the CCD readout
352 time of several milliseconds. For the transmission spectrometer, the
353 intensifier gain was set to 2500 (See [3] for details regarding instrument
354 gain). The gate was set to open at the same time as laser firing by setting
355 the delay to 650 ns relative to an arbitrary start time. The intensifier gate
356 (exposure duration) was 10 μ s, and the CCD exposure duration was
357 4.9834 ms to allow time for the intensifier phosphor glow to decay before
358 transferring data. Additional details of the instrument operation are
359 provided by Maurice et al. and Wiens et al. [2,3].Description of Standards

360 The SuperCam calibration database comprises 334 samples. Most of the standards used in this
361 library come from the database built for the ChemCam calibration [38]. These standards include
362 powdered geologic materials provided by several laboratories, in addition to those purchased
363 from Brammers and U.S. Geological Survey. A variety of igneous, sedimentary, and
364 metamorphic rock types are represented, as well as multiple mineral types: primary igneous
365 minerals (olivines, pyroxenes, and feldspars of various compositions), carbonates (limestone,
366 dolomite, and aragonite), phyllosilicates (nontronite/smectite, kaolinite), sulfates (gypsum and
367 mixtures of sulfate and basalt), phosphates (apatite, heterosite/purpurite), oxides. These
368 samples are described in detail in [38], and are grouped by different mineralogies in (Table 9 in
369 [3]). Samples were prioritized to cover the expected mineral types in Jezero crater identified
370 from orbital spectroscopy, rock types common on Mars, and compositions found at previous
371 landing sites. An attempt was made to cover the geochemically relevant range for each element
372 (Figure 2) but, for several elements, certain compositional ranges (in particular, high
373 concentrations) are underrepresented, making accurate quantification in these ranges
374 challenging. Additional standards may need to be analyzed to improve the calibration in these
375 ranges.

376 Replicates of the onboard SuperCam Calibration Targets (SCCTs) [8,9] as well as several
377 additional calibration targets that are not onboard the rover are also included in the spectral

378 library. These samples are not pressed powders, but sintered powders that make them more
379 durable. These calibration targets include primary igneous minerals, some standards, some
380 natural rocks (serpentine, chert, carbonates), an apatite, some basaltic mixtures doped in minor
381 elements, and a mixture between a basaltic standard with a sulfate [8,9].

382 A table containing the compositions and other metadata for all targets in the calibration
383 database is included in the supplementary material. The individual .fits files for each of the
384 laboratory observations, as well as a single .csv file containing compositions, metadata, and
385 spectra, are available at the SuperCam PDS archive: [https://pds-
386 geosciences.wustl.edu/missions/mars2020/supercam.htm](https://pds-geosciences.wustl.edu/missions/mars2020/supercam.htm)

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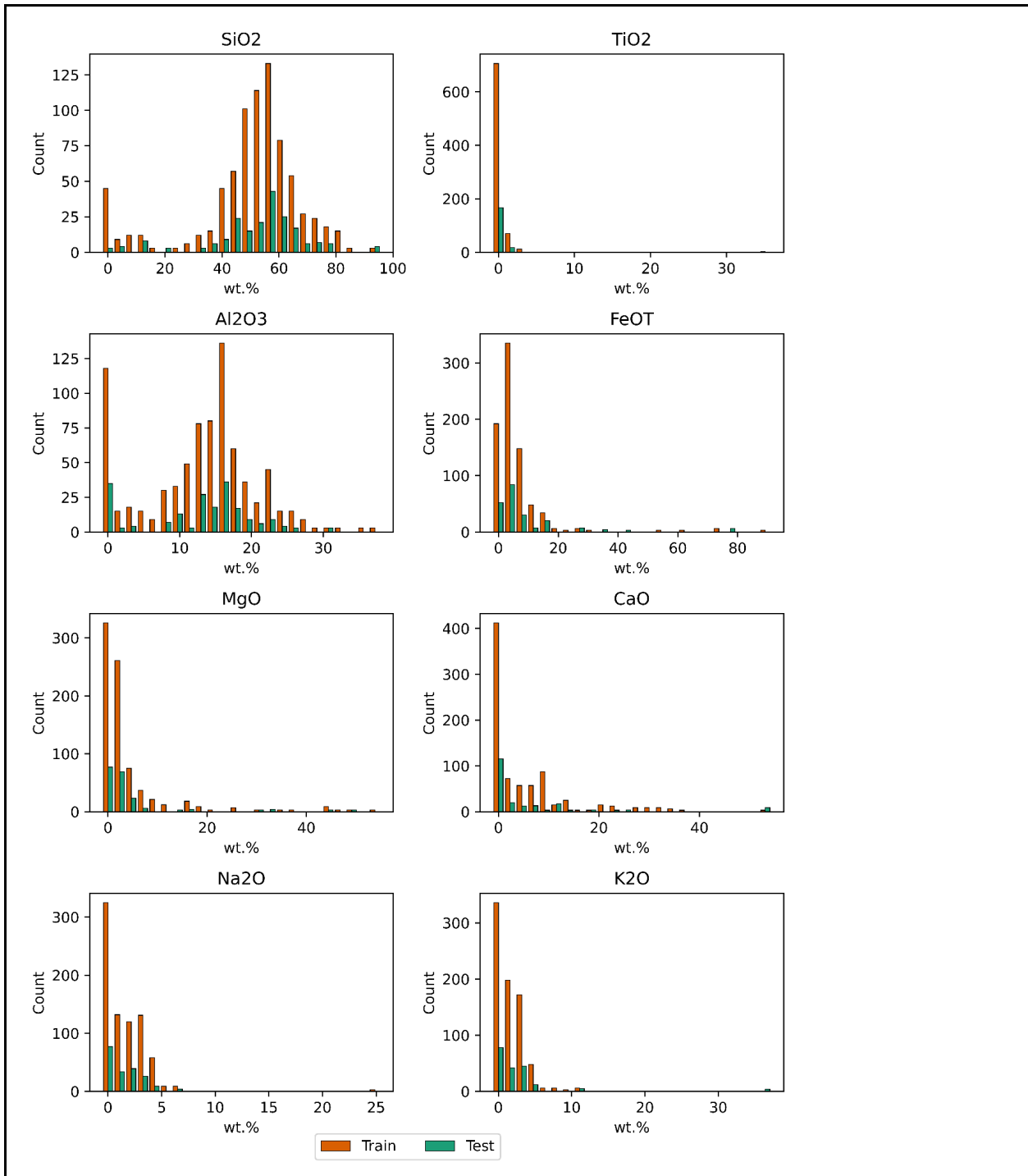


Figure 2: Histograms showing the distribution of compositions in the laboratory data training and test sets for each major element oxide.

394

395

2.2.1. Spectral Variability

397 The performance of our calibration models depends on the diversity of the library of spectra on
398 which they are trained and their similarity to spectra collected on Mars. Given that the spectra
399 have thousands of wavelength channels but the underlying chemical variability is of far lower
400 dimensionality (most natural samples have a small number of major elements, and the emission
401 lines from a given element tend to be highly correlated), we can use dimensionality reduction
402 techniques to simplify exploration of library data and comparison with data from Mars. Principal
403 Component Analysis (PCA; [39–41]) allows us to capture the spectral response to chemical
404 variability by finding a set of only a few principal components that encapsulate most of the
405 variability of the data set. The first step in the PCA process is to compute an $M \times M$ variance-
406 covariance matrix based on the library spectra, where M is the dimensionality of the spectra (the
407 number of spectral channels). This symmetric matrix relates the variability in one wavelength bin
408 to that of all other bins, illustrating their covariance with one another. For example, if Fe content
409 tends to be lower when Si content is higher, it is likely that the covariance of the wavelength bins
410 in those spectral lines/features will have a large negative and positive covariance respectively. If
411 Fe content is independent of Si content, the covariance will be near zero. Once the variance-
412 covariance matrix is computed, an eigenvector decomposition of the matrix is performed, where
413 a set of M linearly independent unit vectors with length M (eigenvectors) are computed and their
414 scalar multiples (M eigenvalues) are computed. In PCA, each eigenvector is sorted according to
415 their eigenvalues and the first few eigenvectors (PCs) reflect the greatest variability in the
416 underlying data set.

417 Before the PCA process, each spectral range was normalized to its respective sum. In Figure 3
418 we show the amount of variance in the normalized library spectra that is represented by the first
419 several components and we show the first two eigenvectors (referred to as ‘loadings’ in PCA) for
420 the UV region of the LIBS spectra. The first two components together explain 60% of the variance
421 in the library spectra and the first ten components explain 95% of the variance. In Figure 4 we
422 show the projection of all library spectra into the principal component space of PC1 and PC2. The
423 maximum extent of the hull or “outline” of the library is defined by a few SCCTs due to their
424 “extreme” pure mineral end-member compositions. Some general compositional groupings and
425 trends can also be identified (Figure 4), for example, with metal oxides and olivines having high
426 PC2 values and carbonates and sulfates, having large PC1 values. These groupings are not strict,
427 and the loadings should be studied for a more detailed understanding of the location of a given
428 spectrum on the scores plot. The clinopyroxene calibration target, for example, is near the
429 (predominantly Ca-bearing) carbonates and sulfates due to their calcium contents. As shown in
430 Figure 3, the first component is strongly correlated with Ca content.

431 To understand whether the library data set encompasses observations on Mars, we plot the PC1
432 versus PC2 scores of all LIBS points acquired in Jezero crater up to
433 Sol (solar day of the mission) 147 in Figure 5 with the hull of the library overlain. Nearly all Mars
434 spectra plot well within the library hull, demonstrating that the extent of the library is likely sufficient
435 in terms of its spectral variability in the dominant components. None of the points that fall outside
436 the hull are dramatically distinct from the library: they do not appear to represent a separate class

437 of materials that would require special analysis. It is worth noting that most of the observations on
438 Mars are centered near the igneous rock compositions, with some notable excursion into end-
439 member compositions at high values in the first two components.

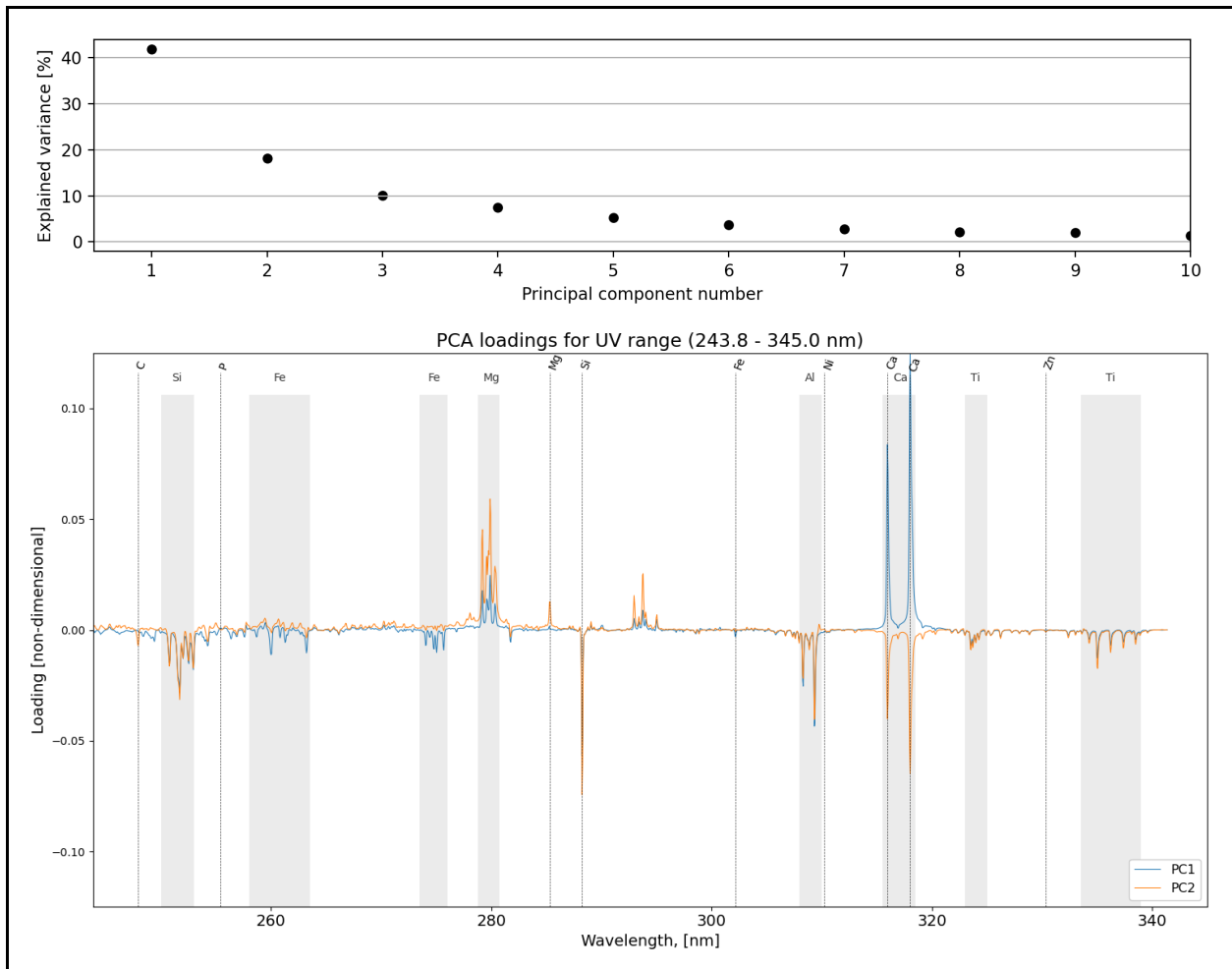


Figure 3: (Top) The amount of variance in the library spectra explained by each principal component. (Bottom) Loadings of the first two principal components across the UV range. The first principal component is strongly correlated with Ca signal and the second is anticorrelated with Ca signal. Both PCs show correlations and anticorrelations in other elements.

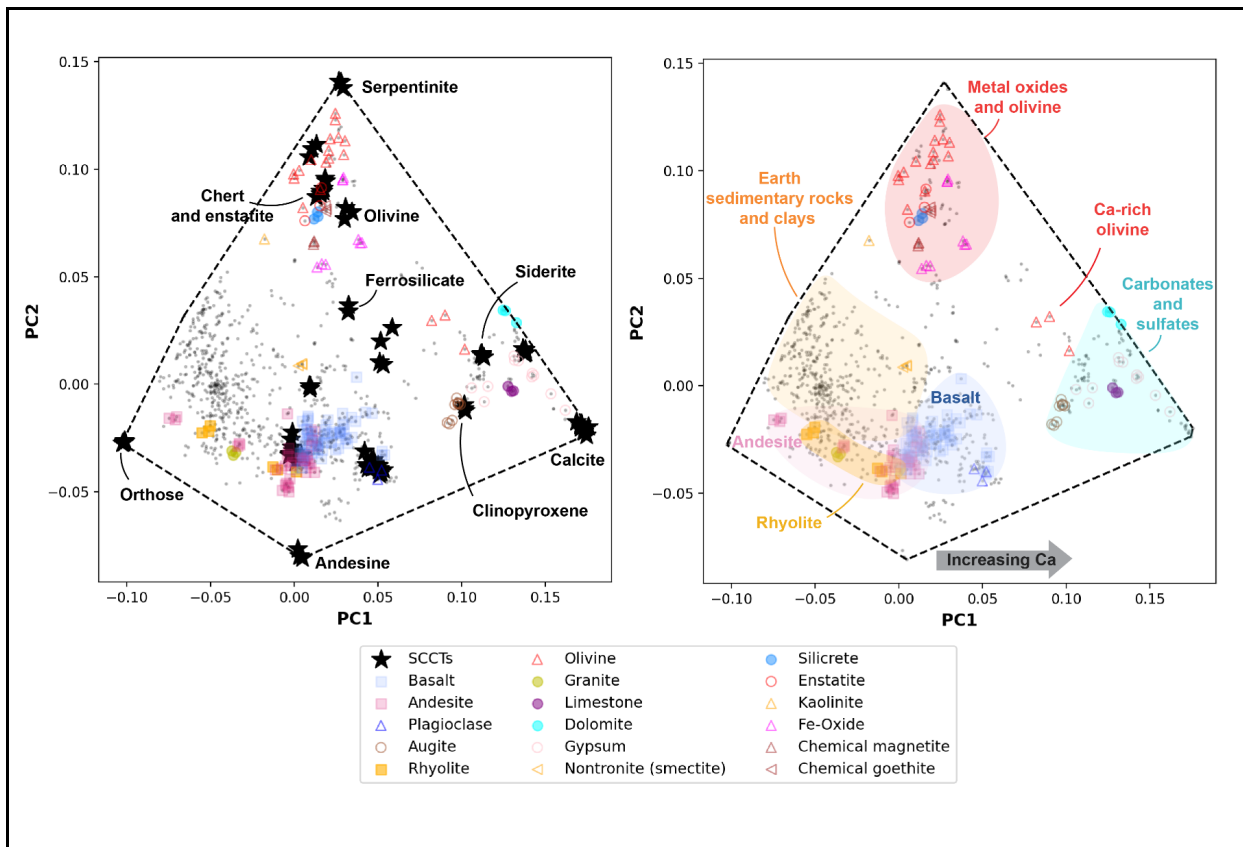


Figure 4: (Left) All library points (grey dots) projected onto the first two PCs with selected sample types denoted by a range of colors and symbols (see legend). Black stars represent SuperCam Calibration Target (SCCT) samples in the laboratory with selected samples labeled. The dashed line represents the convex hull of all the library points. (Right) Same data without the SCCTs highlighted. Groupings of samples are shown by shaded regions, based on the colored symbols, however these regions are not strict. The first principal component is strongly indicative of the calcium line strength in the LIBS spectra.

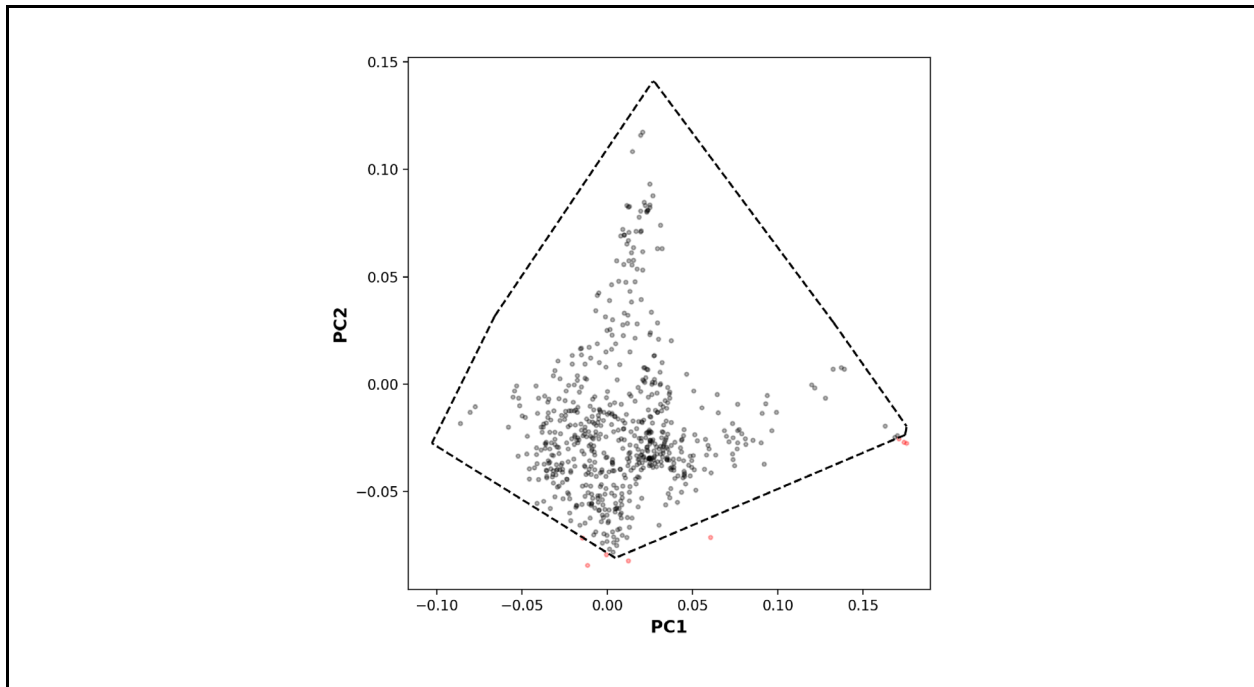


Figure 5: All of the SuperCam LIBS data (circles) from Mars, up to sol 147, projected into the principal component space of the LIBS library (see Figure 4). The convex hull of the library is shown by the dashed line. Only very few observations on Mars fall out of the convex hull of the LIBS library database in this projection (red circles), indicating that the library is generally comprehensive with respect to the LIBS spectral variability observed in targets on Mars.

442 3. Data Processing

443 3.1. Preprocessing

444 3.1.1. Non-laser dark subtraction

445 SuperCam is commanded to take a non-laser “dark” spectrum immediately after the LIBS spectra
 446 using the same spectrometer settings as the active spectrum, but without the laser firing. This is
 447 not a true dark spectrum because light is still falling on the detector, but it serves a similar purpose,
 448 allowing the fixed background signal of the instrument and ambient light to be removed. Signal
 449 and darks for a given observation are stored in the same data file. Dark spectra are averaged and
 450 then the mean spectrum is subtracted from each of the active collects. The dark subtraction also
 451 removes an offset of 300-500 digital numbers (DNs; counts produced by the analog-to-digital
 452 converter in the SuperCam instrument) which is added in the analog-to-digital conversion to
 453 ensure that the converter does not encounter negative values.

454 3.1.2. Stitching

455 In the intensified transmission spectrometer, the light is split into three bands: the band closest
 456 to the CCD serial register is referred to as the “Red” region and covers 707-853 nm; in the

457 center is the “Green” region covering 530-618 nm, and at the other side of the CCD is the
458 “Orange” region covering 598-720 nm[3]. The three bands overlap and are stitched together to
459 obtain a spectrum that has monotonically increasing wavelengths. The transition between
460 spectrometers is selected with two main criteria: 1. Given the choice between two
461 spectrometers, we want to use the higher signal to noise data as indicated by the Instrument
462 Response Function (IRF; see below); 2. To ensure a smooth spectrum, we want to transition
463 between spectrometers in a zone where no emission lines are present. The final spectral
464 channel indices used for the three ranges are listed in Table 1.
465

466 3.1.3. Denoising

467 To remove low level random signal variation across the spectrum (white noise), we use a
468 “stationary” wavelet transform analysis to decompose the spectrum, remove noise, and then
469 reconstruct the spectrum. The stationary wavelet transform is particularly useful for identifying
470 noise [42,43] and the method we use for SuperCam is almost identical to that performed for
471 ChemCam data reduction [44].

472 Wavelet analysis involves a convolution of the signal with orthogonal basis functions (wavelets)
473 that have both scale and frequency properties. The process results in an invertible transform that
474 can be considered as a series of band pass filters with a response function that is uniform in
475 shape (a constant-shaped wavelet) but variable in scale and frequency. Using the orthogonality
476 properties of the basis function, a spectrum can be completely characterized by the wavelet basis
477 function and associated coefficients determined through the decomposition process.

478 A scaling function $\phi(x)$ and a wavelet function $\psi(x)$ are used for the wavelet transform. The
479 continuous scaling function satisfies the following equation:

$$480 \quad \phi(x) = \sqrt{2} \sum_n h(n) \phi(2x - n)$$

481 where $h(n)$ is the low-pass filter, x are the spectral channels, and n is the level of the wavelet
482 decomposition.

483 The continuous wavelet is defined in terms of the scaling function and the high-pass $g(n)$ QMF
484 through:

$$485 \quad \psi(x) = \sqrt{2} \sum_n g(n) \psi(2x - n)$$

486 In the standard “discrete” wavelet transform (DWT), the input signal is broken down into a series
487 of decomposition levels. At each level L , the wavelet has a resolution reduced by a factor of 2^L
488 with respect to the original signal. That is, if the signal is defined across 100 nanometers, at level
489 $L=2$, the wavelets will have a length of $100/2^L$ or 25 nanometers. At each level, the wavelet
490 decreases in size, providing greater resolution of high frequency or sharper spectral features
491 (Figure 6).

492 One downside to the discrete wavelet transform that is relevant to spectral noise characterization
493 is that all levels are required in the reconstruction of the signal (i.e. the levels are “non-redundant”)
494 and the loss of the translation-invariance property in the DWT leads to a large number of artifacts
495 when a signal is reconstructed after modification of its wavelet coefficients. This is undesirable for
496 denoising because the goal is to isolate the noise, remove it, and reconstruct the signal without
497 noise. We instead use a stationary or undecimated form of the wavelet transform [45] in which
498 each level is redundant, with higher levels containing information necessary to deconstruct the
499 signal in the previous level. Thus, in the context of spectral analysis, the levels can be inspected
500 to distinguish between salient features, e.g., emission lines and white noise. We direct the reader
501 to [46] for a mathematical description and a comparative discussion of discrete and stationary
502 wavelet analysis for an analogous noise characterization analysis.

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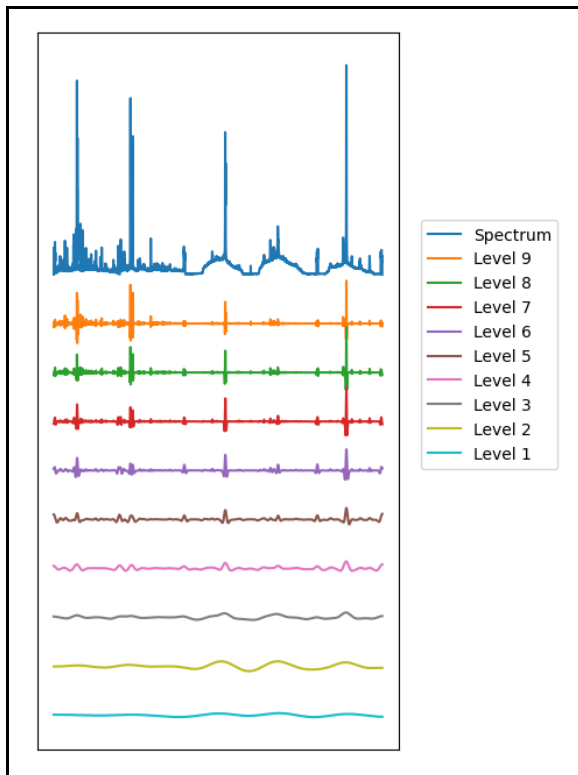


Figure 6: Illustration of the wavelet decomposition of a LIBS spectrum, with vertical offset applied to each level. Horizontal axis is wavelength, vertical axis is intensity. Numerical values are omitted because the decomposition is applied prior to wavelength calibration or conversion to physical units.

505

506 In our application of the stationary transform, the wavelet coefficients are found by calculating the
507 difference between two successive scaling passes. The scaling function used is a B₃-spline, and
508 the associated low-pass filter h is defined in terms of its z-transform as:

$$509 \quad h(z) = 1/16(z^{-2} + 4z^{-1} + 6z^0 + 4z^1 + z^2)$$

510 We use the second generation of the transform described by [45] which is more robust to artefacts
511 than other wavelet-based denoising methods. The z-transform of the high-pass filter g is:

$$512 \quad g(z) = 1/256(-z^4 - 8z^3 - 28z^2 - 56z^1 + 186z^0 - 56z^{-1} - 28z^{-2} - 8z^{-3} - z^{-4})$$

513 This differs from the high-pass filter used in [44]:

$$514 \quad g(z) = 1/16(-z^{-1} - 6z^0 + 16z^1 + 6z^2 + z^3)$$

515 For more details on the stationary wavelet transform and its implementation, refer to [45].

516 At each scale, noise is identified and removed using “sigma clipping” as described in [47,48]. We
517 calculate the standard deviation of the absolute value of the wavelet spectrum at a given
518 decomposition scale and identify those spectral channels with values less than three times the
519 standard deviation. This process is repeated iteratively on the channels that fall below the
520 threshold several times to arrive at an estimate of the standard deviation of the noise in the
521 wavelet spectrum at each scale. Then, values in the wavelet spectrum below three times the
522 standard deviation are set to zero. Once this has been applied to each scale of the wavelet
523 decomposition, the de-noised spectrum is reconstructed by summing the wavelet scales.

524 Figure 7 illustrates the result of denoising applied to a spectrum acquired on Mars. The figure
525 shows a small subset of the spectrum so that the noise and the difference between the original
526 and denoised spectrum can be seen. The average absolute change in signal for this spectrum
527 after denoising is ~8 DNs.

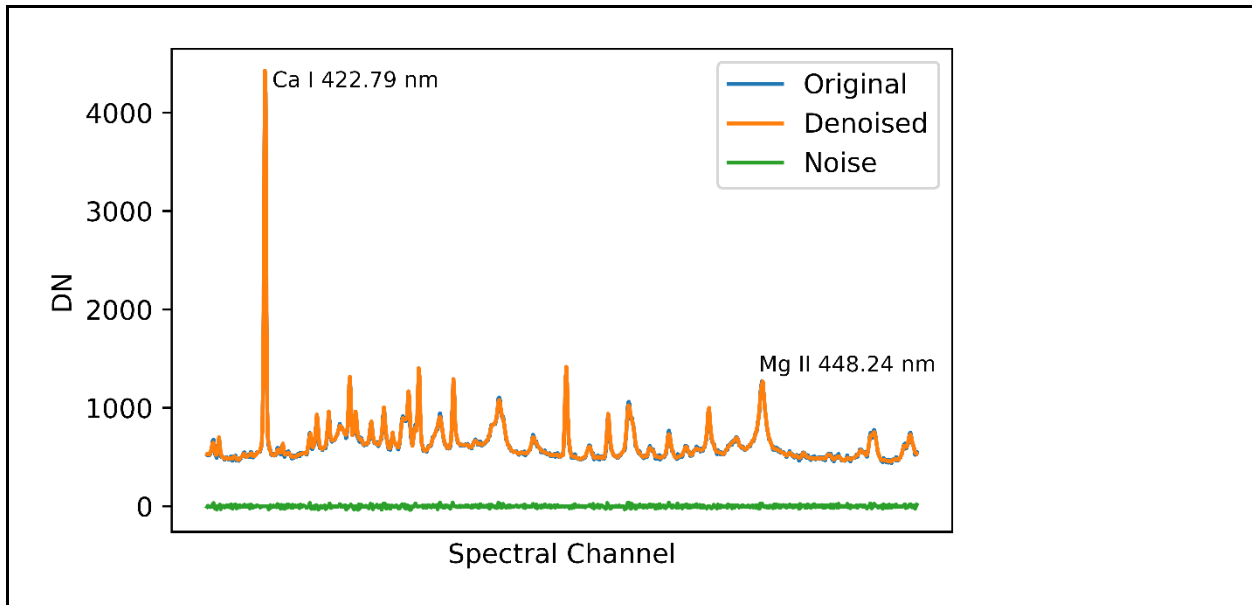


Figure 7: Example illustrating the effect of denoising. This figure shows a subset of the EDR spectrum of the target Máaz, in the 420 - 450 nm range. Vertical axis is intensity, horizontal axis is wavelength. Denoising is applied prior to wavelength calibration so we omit the numerical values on the x axis. The two strongest emission lines in this range are labeled.

528 3.1.4. Instrument Response Function and Conversion to Radiance

529 SuperCam spectra are converted to physical units of radiance ($W/cm^2/sr/nm$) prior to quantitative
 530 analysis. The conversion from photons to radiance is similar to that described in section 2.3.4 of
 531 [44]. First, the recorded CCD signal in DN (digital number) is converted to photons using the
 532 Instrument Response Function (IRF).. Figure 8 shows the IRF for the three spectrometers. After
 533 the IRF has been applied, the spectrum is divided by the integration time, area on target, solid
 534 angle subtended by the telescope, and spectral channel width for each CCD column. Finally,
 535 photons/s is converted to watts using $E = hc/\lambda$ for each spectral channel. The calculation of both
 536 the area of the target visible from the telescope and the solid angle subtended by the telescope
 537 as seen from the target include the distance to the target, so applying the conversion to radiance
 538 includes an implicit correction for distance for the light emitted by the plasma spark.

539
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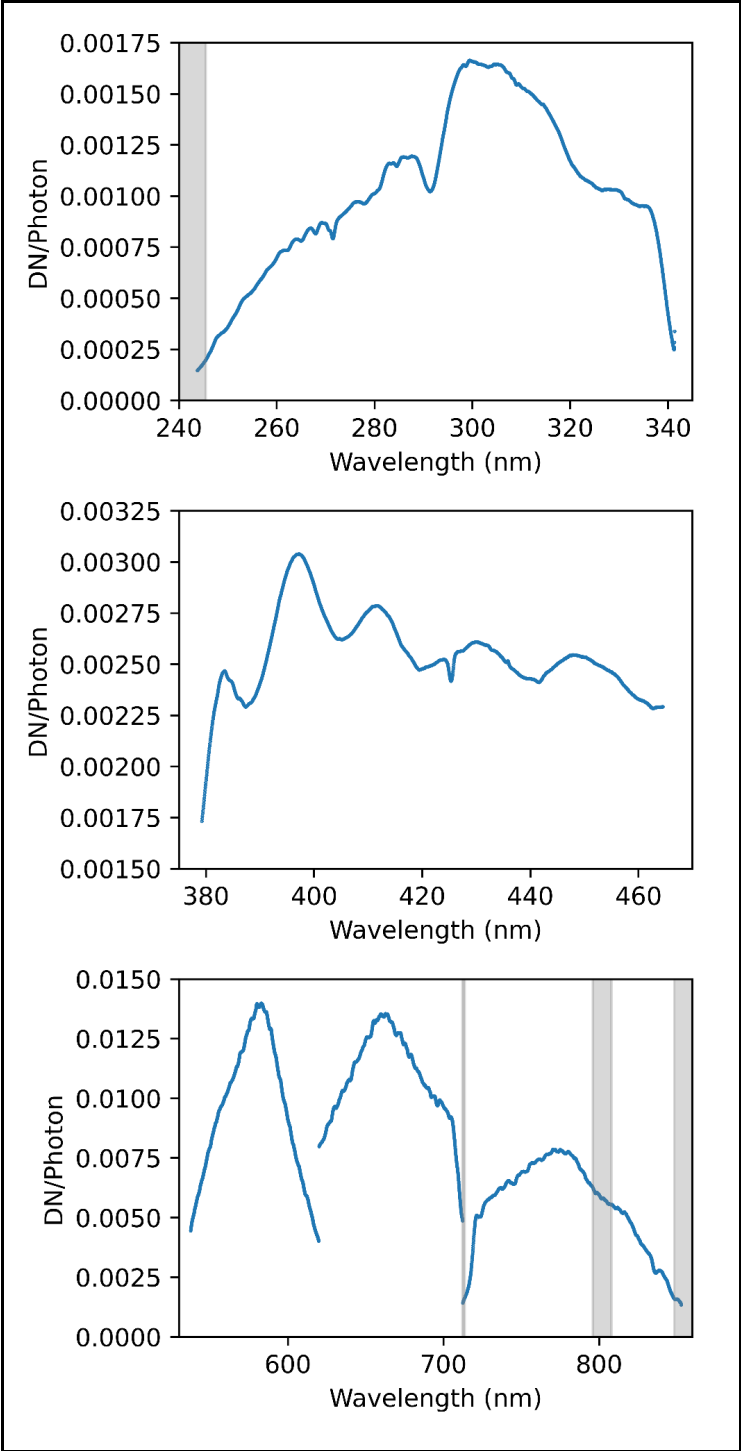


Figure 8: SuperCam instrument response function (IRF) for the three spectrometers. Gray rectangles indicate portions of the spectrum that are masked before quantification (see the “Additional Preprocessing for Quantification” section).

542

3.1.5. Continuum Removal

543 Laser-induced plasma emission contains a background continuum due to primarily to ion-electron
544 recombination processes. In SuperCam spectra, this is most notable in the three transmission
545 spectrometers. This continuum shows some correlation with chemical composition [49,50], but is
546 more strongly influenced by the amount of laser energy absorbed by the target (e.g. due to
547 distance or focus). We have found that removing the continuum prior to normalization helps to
548 mitigate these variations. We use the same continuum removal procedure described by [44].

549 The continuum removal algorithm is based on the same wavelet decomposition as the de-noising
550 algorithm described above. It works by decomposing the spectrum to a specified scale and then
551 finding the local minima of the decomposed spectrum at that scale. Then, minima are found in
552 the original input spectrum within windows of $\pm 2^L$ around each local minimum from the
553 decomposed signal, where L is the wavelet scale. A cubic spline is fit to these minima and
554 subtracted from the input spectrum. For each wavelet scale, beginning with the largest scale and
555 continuing to lower scales until reaching a specified minimum scale, the process is repeated
556 iteratively until the standard deviation of the corrected spectrum stops changing significantly or a
557 maximum number of iterations is reached. The advantage of this algorithm is that it is fast and
558 relies on very few parameters. Figure 9 illustrates how the removed continuum evolves with each
559 additional scale.

560

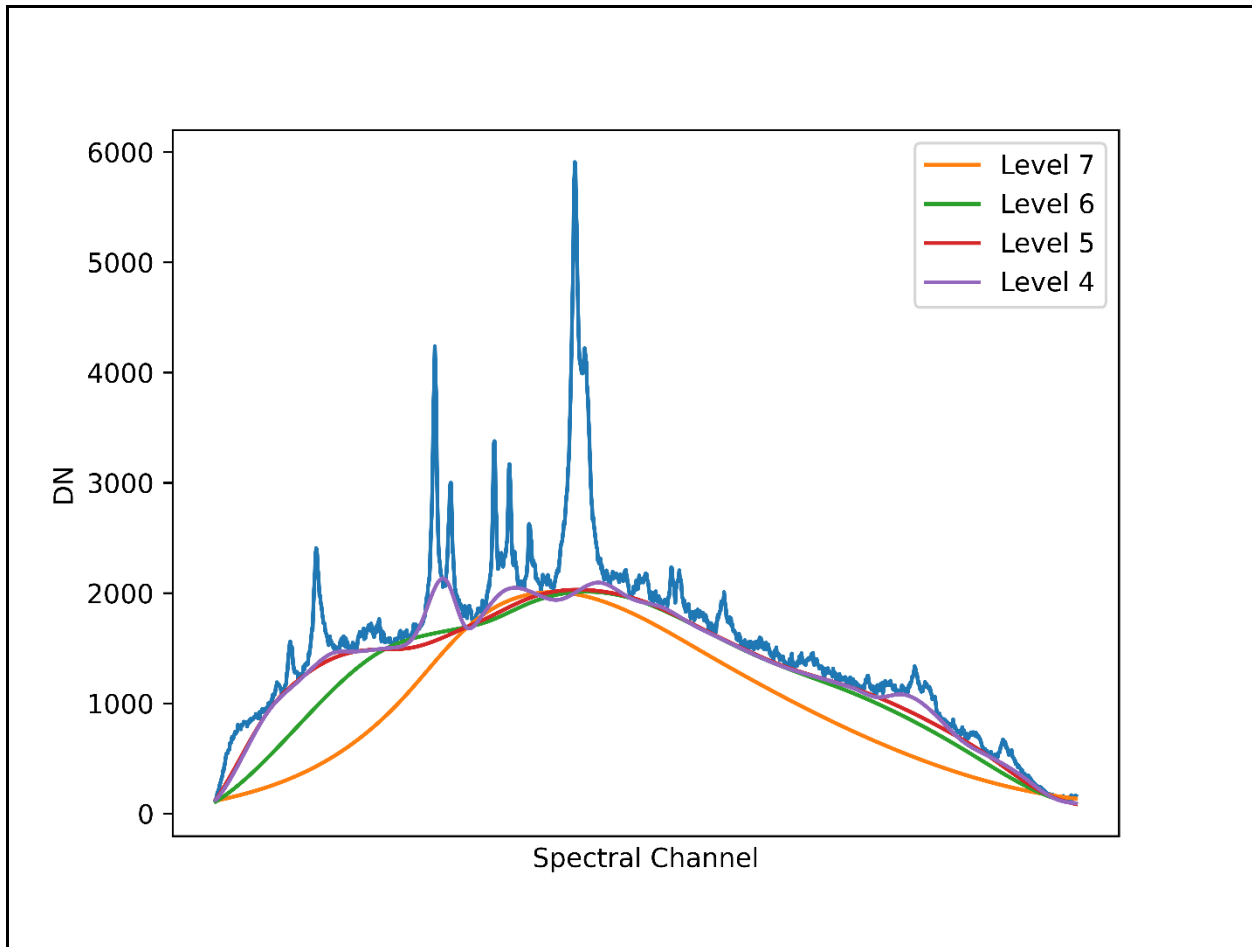


Figure 9: Illustration of how reducing the minimum wavelet scale results in a continuum which more closely follows small-scale variations in the spectrum. The level 4 continuum fits the spectrum too closely, while the continuum at levels 6 and 7 does not fit closely enough. This figure shows a subset of the Orange spectrometer. Wavelength values are omitted from the x axis because continuum removal is applied prior to wavelength calibration.

561

562 The default parameters for the minimum wavelength scale for continuum removal are 6 for the
 563 UV and VIO spectral ranges, and 5 for the three transmission spectrometer ranges (Green,
 564 Orange, Red). Increasing this parameter produces a smoother continuum, but a lower number
 565 gives a continuum that follows the spectrum more closely (Figure 9).

566 3.1.6. Wavelength Calibration

567 Wavelength calibration is performed by comparing the spectrum to be calibrated with a
 568 reference spectrum. The reference spectrum can be either a real spectrum acquired by the
 569 instrument or a synthetic spectrum built from lines of interest. In either case, the known
 570 positions of the emission lines are mapped to spectral channel indices using a pattern
 571 recognition algorithm, and a continuous wavelength distribution is fit to these index-wavelength
 572 pairs. The procedure is an updated version of the method described in section 2.3.3 of [44]. We

573 use the vacuum wavelengths of the emission lines from the NIST spectral database [51] rather
574 than the wavelengths in air at 1 bar because all data were acquired at martian atmospheric
575 pressure (6 mbars).

576
577 The UV and VIO ranges of the calibration database are calibrated against a spectrum acquired
578 on a titanium plate. Titanium is well suited for the UV and VIO ranges because it contains a
579 large number of emission lines in these ranges. For the Green, Orange and Red spectrometers,
580 we used synthetic spectra built with emissions lines of identified elements in the respective
581 ranges. The wavelength calibration of the laboratory database serves as a reference for all the
582 spectra acquired on Mars.

583
584 Wavelength calibration for the flight instrument was calculated using LIBS spectra from a
585 titanium plate and two additional targets: IlmHem which is a mixture of ilmenite and hematite,
586 and ClinQzOrth which is a mixture of clinozoisite quartz and orthoclase. These spectra were
587 collected during the rover System Thermal Test in October 2019. Because wavelength
588 calibration alters the distance in wavelength space covered by each channel, we re-sample the
589 calibrated spectrum onto the baseline channel-to-wavelength map. Finally, the spectra are re-
590 interpolated over the reference wavelength defined for the calibration database so that the
591 wavelengths of the Mars and laboratory data have precisely the same wavelength values.

592
593 On Mars, we observe slight changes in wavelength calibration as a function of temperature.
594 Figure 10 shows the average absolute pixel (spectral channel) shift calculated for the UV and
595 VIO ranges for all active LIBS sequences taken up to sol 147 of the mission. The median of the
596 average shift is 0.16 pixel for the UV range, and 0.2 pixel for the VIO range. All values remain
597 well within ± 0.5 pixel shift in the UV range, and within ± 1 pixel shift for the VIO range. The
598 transmission spectrometer calibrations have been checked to be robust to temperature
599 variations and typically present an average shift of about 0.02 pixels per degree, much lower
600 than for the UV and VIO ranges. Given the small observed shifts, the wavelength calibration for
601 SuperCam spectra is not currently adjusted for temperature.

602

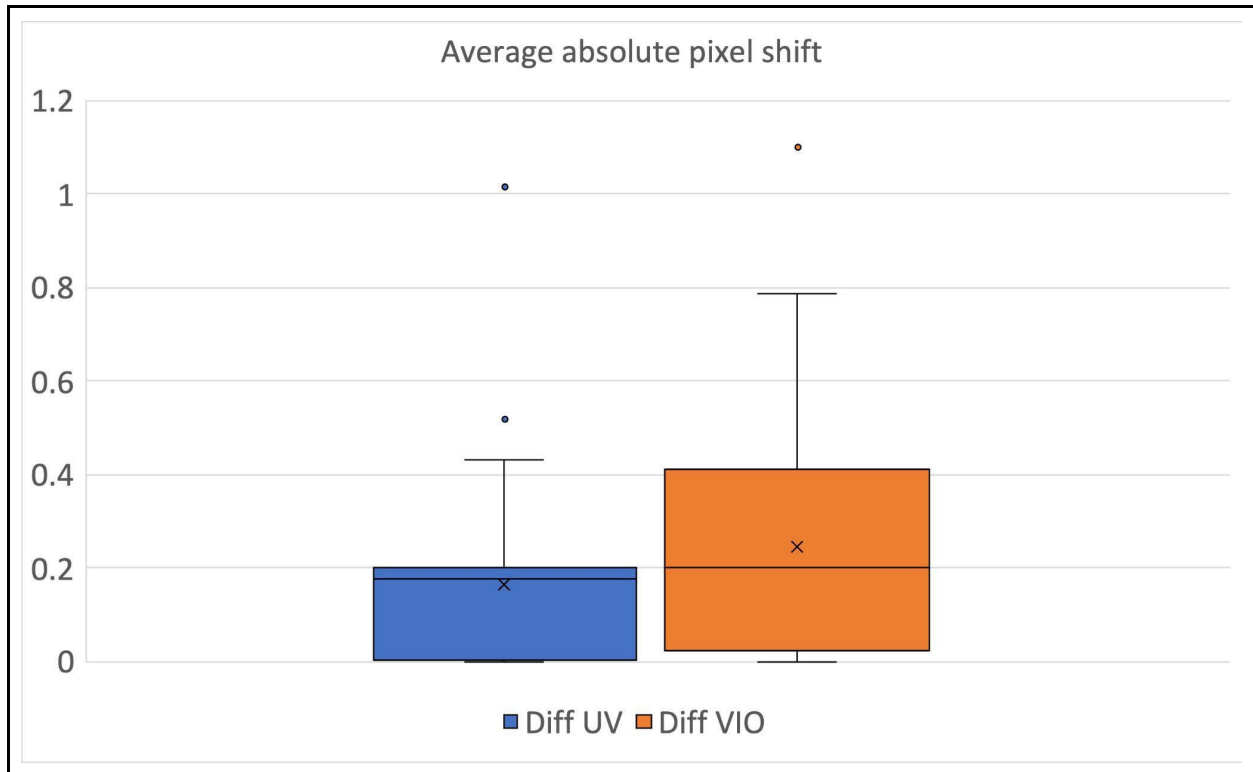


Figure 10: Boxplot of the average absolute pixel shift detected for all SuperCam active LIBS sequences up to sol 147 on Mars. The average shift calculated for these spectrometers remain well within +/- 1 pixel. The transmission spectrometer exhibits a much smaller shift than the UV and VIO spectrometers.

603

604

3.1.7. Additional Preprocessing for Quantification

605

In addition to the preprocessing applied to all spectra, we also applied several additional steps prior to training regression models. The first is masking: to ensure that quantification is based on the highest-quality data, we defined a mask to remove portions of the spectra with lower signal to noise, based on investigation of the instrument response function (Figure 8), while also retaining key emission lines, such as the Ti lines at the long-wavelength end of the UV range. We masked out the UV spectrometer for wavelengths less than 245.5 nm and the Red spectrometer for regions where the instrument response is $<1/5$ the best instrument response value for the Red spectrometer. This results in the removal of Red spectrometer data between 712.17 nm and 714 nm, and for wavelengths >848.3 nm. No masking was required for the VIO, Green, or Orange spectrometers. There was also an anomalous feature in some of the laboratory data in the wavelength range $796 \text{ nm} \leq \lambda \leq 808 \text{ nm}$ that was masked.

616

We also normalized each spectrum. This involves dividing the portion of the spectrum from each spectrometer by the total signal from that spectrometer. We treat the three spectral ranges of the transmission spectrometer separately, so we have five spectral ranges for normalization.

618

619

Thus, after normalization is applied, the full spectrum across all five spectral ranges sums to 5.

620 Normalization helps to mitigate fluctuations in signal between observations and partly reduces
621 the effect of distance on the spectrum.

622 We also experimented with applying standardization and peak binning to the spectra. Peak
623 binning is an algorithm originally developed for ChemCam analysis as a fast and simple
624 alternative to fitting and summing all of the individual peaks in a spectrum [52]. It works by
625 calculating an average training set spectrum and using that average spectrum to identify the
626 wavelength values of local minima and local maxima. Each individual spectrum is then binned:
627 the signal between pairs of local minima is summed, and the resulting value is assigned to the
628 wavelength of the local maximum. In this way, the full spectrum (>7900 spectral channels after
629 masking) can be replaced with a “spectrum” of summed values (~560 channels). This has the
630 benefit of significantly reducing the size of the spectrum and collecting the signal from each line
631 into a single value, increasing robustness to small shifts in wavelength calibration. Peak binning
632 may also increase model sensitivity to broad or weak lines [52]. We applied peak binning prior
633 to normalization. Regression models with and without peak binning were evaluated for all
634 elements, but it did not always improve the accuracy of the quantification.

635 Standardization involves subtracting the average value and dividing by the standard deviation
636 for each spectral channel, resulting in a spectrum where each channel has a mean value of 0
637 and a standard deviation of 1. The mean and standard deviation are calculated based on the
638 training set spectra, and the same values are used to standardize unknown spectra to be
639 predicted. Standardization can help with regression in some cases by equalizing the influence of
640 all spectral channels on the model. It reduces the magnitude of very bright emission lines and
641 amplifies portions of the spectrum with few or weak emission lines. The resulting spectra and
642 regression coefficients are less intuitive for human interpretation but can lead to improved
643 regression models. Standardization was applied after normalization. As with peak binning, we
644 evaluated models with and without standardization for each of the major elements, but it did not
645 always improve the results.

646 We also shifted the wavelength calibration of the training spectra by ± 1 to 3 pixels and used
647 both the shifted and unshifted data to train models. The observed variation in wavelength
648 calibration on Mars is small (Figure 10), but we found that models trained on shifted spectra did
649 not suffer in performance when predicting unshifted data but were more robust to shifts in
650 wavelength if they were to occur, so most of the models considered were trained on spectra
651 with shifts of up to 1 or 2 pixels.

652 3.2. Data Organization

653 One challenge for developing an empirical multivariate calibration is determining the optimal
654 parameters to use for the regression algorithms considered. Many algorithms are susceptible to
655 “overfitting” - tuning the parameters such that the model performs well on the training set but
656 does not handle novel data well. To tune model parameters while avoiding overfitting, we use k-
657 fold cross validation [53] in which the data are split into k roughly equal-sized parts or “folds.”
658 We used five folds, defined separately for each major element. The exact number of folds used
659 has been shown to have little effect on the performance of the final model as long as both the

660 training set and test set provide a good representation of the sample variability [54]. We
661 “stratified” the data by sorting on the abundance of the element of interest, so that when the
662 samples are sequentially assigned to the folds, the result is that the distribution of compositions
663 is as similar as possible (Figure 11). This helps to reduce the likelihood that all of the samples
664 with the highest concentration of the element being predicted do not end up in one fold, causing
665 it to behave dramatically differently than the other folds. To some extent this situation is
666 unavoidable, given the “long tail” of higher compositions for many elements, but stratification
667 minimizes the effect. All spectra of the same target are grouped together when defining the
668 folds to ensure that the folds are independent

669 We held out one of the folds as a “test set” which is used for model selection and estimation of
670 accuracy only after cross validation and model tuning have been completed. All rover calibration
671 targets were kept in the test set so spectra from Mars can be used to assess model
672 performance.

673 The cross-validation process involves stepping through the remaining four folds, holding out one
674 at a time, training a model based on the other three folds, and predicting the held-out data. This
675 gives an estimate of how the final model, trained on all four folds in the training set, will perform
676 on unknown data. The optimum parameters for a given algorithm can be determined by
677 examining how the root mean squared error of cross validation (RMSECV) varies with different
678 settings. When the RMSECV is similar for multiple different settings of a model, the least-
679 complex model was adopted.

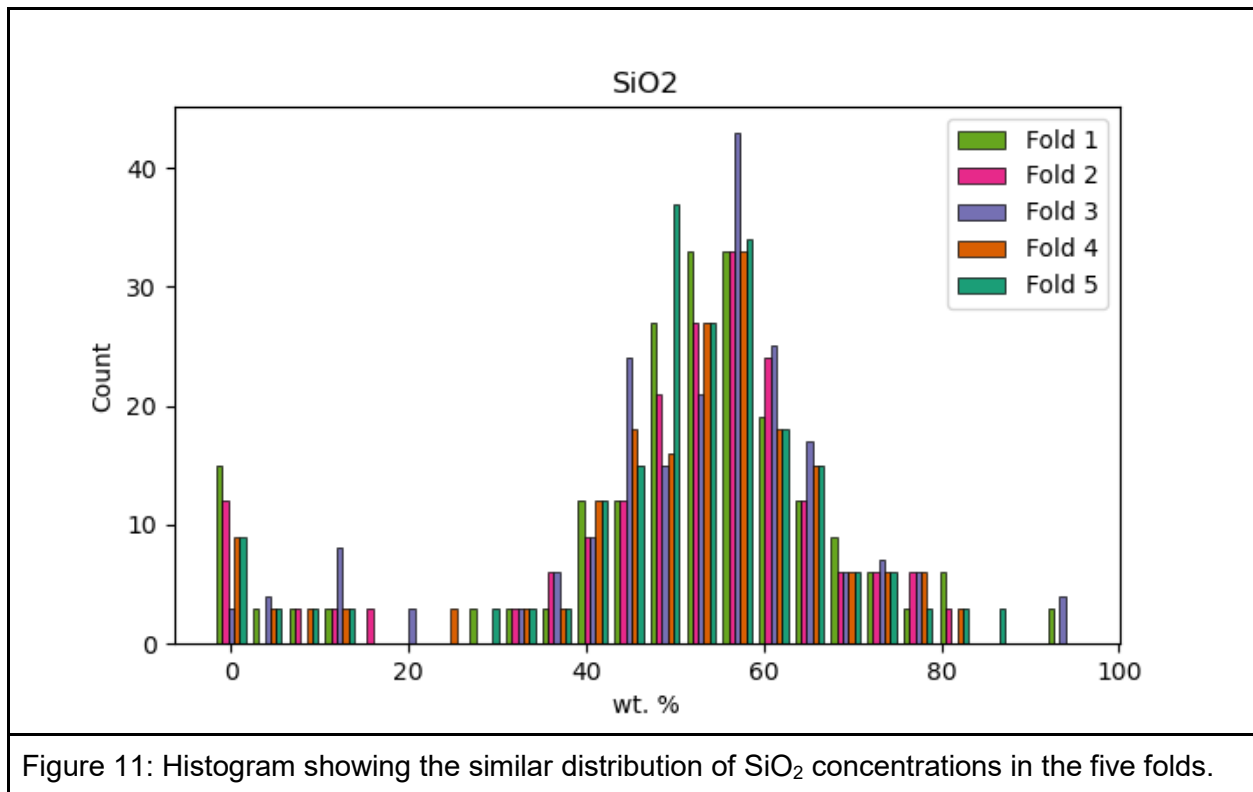


Figure 11: Histogram showing the similar distribution of SiO₂ concentrations in the five folds.

3.2.1. Outlier Removal

681 We use several approaches to determine whether certain samples should be considered
 682 “outliers” in the development of our models for each element. First, we evaluate the data quality
 683 to determine if each spectrum is valid to use at all. Some spectra exhibit low total signal, low
 684 signal to noise, and anomalous curvature in the continuum of the UV spectrometer and are
 685 marked for potential removal, although they were not removed until after the outlier identification
 686 steps described here were applied.

687 We next evaluate target homogeneity by running a PCA analysis on the full data set and
 688 qualitatively inspecting the PC1 vs PC2 score plots to visualize how tightly grouped the points
 689 for a given target were. This analysis allowed us to remove several anomalous spectra. In other
 690 cases, the points for a given target exhibited considerable variation on the scores plot. If one
 691 point was significantly different from the others, it was removed while the homogeneous points
 692 were kept. In cases where all spectra from a target showed significant scatter, we took this as
 693 an indication that the target was not sufficiently homogenized during preparation; thus, the
 694 reference composition may not match the composition of the spots analyzed. For these cases,
 695 all spectra for the target were removed.

696 We also used several outlier identification approaches to more quantitatively identify potentially
 697 problematic spectra. Two of these were algorithms available through the scikit-learn Python
 698 library: local outlier factor (LOF) and isolation forest (IF) [55,56]. LOF works by calculating the
 699 distance from each spectrum to its nearest neighbors and comparing with the average distance
 700 to the nearest neighbors of the nearest neighbors. Outliers are expected to be farther from their
 701 neighbors than average. IF works by randomly splitting the high-dimensionality point cloud of
 702 spectra until the spectrum of interest is isolated. An outlier tends to require relatively few splits
 703 to isolate, while a spectrum that is more “typical” will be in the dense part of the cloud and
 704 require more splits to isolate. We ran both algorithms on the normalized spectra, with
 705 parameters set so that they would flag 10% of the spectra as potential outliers. We then
 706 removed those spectra that were flagged by both methods. Many of the spectra flagged by LOF
 707 and IF as potential outliers were also identified above as having low signal.

708 Another approach to outlier identification is to generate a partial least squares (PLS) model and
 709 plot the Q residuals against the Hotelling T^2 values for each spectrum. For this, we used
 710 PLS_toolbox 8.9 (Eigenvector Research Inc.) for MATLAB R2020b (MathWorks Inc.). For a
 711 model that represents the spectra X using loadings P and scores T , with an error matrix E

$$712 \quad X = TP^T + E$$

713 Q residuals are defined as

$$714 \quad Q_i = e_i e_i^T = x_i (I - P_k P_k^T) x_i^T,$$

715 where e_i is the error for the i th spectrum, x_i is the i th spectrum, I is the identity matrix, and P_k are
 716 the loadings for the k components of the model. Q_i is a summary of how well the selected

717 components model the spectrum, with larger values indicating a spectrum that is not handled
718 well by the model.

719 Hotelling's T^2 statistic is defined as

$$720 \quad T_i^2 = t_i \lambda^{-1} t_i^T = x_i P_k \lambda^{-1} P_k^T x_i^T$$

721 where t_i refers to the i -th row of the scores matrix T , and λ is the matrix of eigenvalues
722 corresponding to the k of components in the model. T_i^2 reflects the leverage of a spectrum on
723 the model.

724 Outliers on the Q vs T^2 plot are points that plot far away from the origin, particularly those with
725 high values of both Q and T^2 , indicating that the spectrum has a significant amount of influence
726 on the model (high T^2) but is still poorly predicted by the model (high Q).

727 A similar approach to calculating Q is to train a PLS model and identify training set samples that
728 are poorly predicted by the model. For each major element, we used both the Q vs T^2 and the
729 training set approach and flagged potential outliers. Spectra flagged as outliers for many or all of
730 the major elements using these two model-based methods were removed completely from all
731 models. These spectra included ilmenite, a mix of quartz and cobaltite, a Mn oxide, and
732 sodalite. If these model-based methods flagged a spectrum as an outlier for only a small
733 number of the major elements, then that spectrum was removed for those elements but kept for
734 other element models.

735 One of the challenges of defining outliers is how to handle high-quality spectra from samples
736 that are very different from the average. In our data set, these tend to be mineral samples with
737 unusually high concentrations of one element. These spectra may be flagged as outliers
738 because they are either poorly modeled or they exert an undue influence on the model, but they
739 are valid data and may improve the model performance at high concentrations at the expense of
740 the performance at low concentrations. Thus, we found it useful to handle these samples
741 differently depending on the model being trained. We remove them from fixed models intended
742 to accurately predict low concentrations but retain them for models restricted to high
743 concentrations, and for local regression models, which dynamically adjust the samples being
744 used to match the unknown spectrum (see below). To define which samples should be handled
745 in this way, we established a threshold for compositions to be considered "high" compared to
746 the rest of the data set. For each element, we calculated the median and standard deviation of
747 the composition across all standards in the database. Standards were considered "high"
748 concentration if they had values greater than 1 standard deviation above the median value.
749 Spectra that were both "high" in composition based on this criterion and flagged as outliers were
750 removed when training models intended to predict the full range (0-100 wt.%) for an element but
751 were kept for high-concentration submodels and local regression models. In total, out of 1198
752 individual spectra, 54 were removed from all major element models. The number of spectra
753 removed for each of the major elements is listed in Table 2. For "high" models, fewer spectra
754 are removed because those identified as high concentration are retained.

Table 2: Outliers removed from laboratory data set

	# of Outlier Spectra	# of Outlier Spectra (for “High” models)
SiO ₂	102	92
TiO ₂	114	112
Al ₂ O ₃	101	89
FeO _T	102	94
MgO	97	78
CaO	125	100
Na ₂ O	120	116
K ₂ O	115	97

755 **4. Quantification**

756 4.1. Algorithms

757 No single multivariate regression algorithm is clearly the best choice for all major elements. For
 758 our work toward a quantitative prediction model for each major element, we take the approach
 759 of trying a wide variety of algorithms and choosing the model or models that give the best
 760 results. We first discuss the algorithms in this section and in the next section we discuss the
 761 criteria used to select the preferred model. The algorithms considered are listed in Table 3. We
 762 used the Python library scikit-learn [57] to implement these algorithms.

Table 3: Regression algorithms and abbreviations

Algorithm	Abbreviation
Ordinary Least Squares	OLS
Partial Least Squares	PLS
Least Absolute Shrinkage and Selection Operator	LASSO
Ridge regression	Ridge
Elastic Net	ENet
Orthogonal Matching Pursuit	OMP
Support Vector Regression	SVR

Random Forest	RF
Gradient Boosting Regression	GBR
Local Elastic Net	Local ENet
Blended submodels	Blend

763 Ordinary Least Squares (OLS) is the simplest approach to multivariate regression. For the n
764 spectra x with p spectral channels, it seeks to find the regression coefficients w to predict the
765 composition y :

$$766 \quad y_{i,predict} = w_0 + w_1x_{1i} + w_2x_{2i} + w_3x_{3i} + \dots + w_px_{pi}$$

767 while minimizing the sum of squared residuals:

$$768 \quad \sum_{i=0}^n (y_{i,predict} - y_{i,true})^2 = \sum_{i=0}^n (x_iw - y_{i,true})^2$$

769 OLS tends to perform poorly when there is a high degree of correlation between the features in
770 the data, which is a common situation when working with spectroscopic data. However, we
771 included OLS as a point of comparison for other more sophisticated algorithms.

772 Least Absolute Selection and Shrinkage Operator (LASSO; Tibshirani, 1996) is one of several
773 methods that seek to improve upon OLS by adding a “regularization” term, which seeks to
774 impose constraints or certain behaviors on the regression model. LASSO adds a term
775 consisting of a constant (α) multiplied by the sum of the absolute values of the regression
776 coefficients w .

$$777 \quad \sum_{i=0}^n (x_iw - y_{i,true})^2 + \alpha \sum_{j=0}^p |w_j|$$

778 Minimizing this regularized equation has the effect of simplifying the model by setting many of
779 the regression coefficients to zero. The value of α adjusts how strongly the regularization term is
780 weighted, and therefore how sparse the solution is. A sparse model has the benefit of being
781 easier to interpret and potentially faster, while still performing well [59].

782 Ridge regression [60] imposes a different form of regularization to the model, the sum of the
783 squares of the regression coefficients:

$$784 \quad \sum_{i=0}^n (x_iw - y_{i,true})^2 + \alpha \sum_{j=0}^p w_j^2$$

785 This has the effect of penalizing models in which certain coefficients are significantly larger than
786 the others, which in turn can make the model more robust to correlation between x variables
787 (spectral channels)

788 Elastic Net (Enet; [61]) combines the Ridge and Lasso regularizations, using the parameter ρ to
789 control their relative strengths:

$$790 \quad \sum_{i=0}^n (x_i w - y_{i,true})^2 + \alpha(1 - \rho)/2 \sum_{j=0}^p w_j^2 + \alpha\rho \sum_{k=0}^p |w_k|$$

791 Orthogonal Matching Pursuit (OMP) [62,63] seeks to minimize the least squared error, with a
792 constraint on the total number of non-zero regression coefficients. It iteratively selects spectral
793 channels, with each additional channel chosen to be orthogonal to previously selected channels
794 and highly correlated with the remaining residual.

795 Partial Least Squares (PLS; [63]) is a regression method that is closely related to PCA and has
796 previously been used successfully for LIBS calibration (e.g., [37,43,64,65]). Like PCA, PLS
797 seeks to reproject high-dimensionality data (spectra) into a lower-dimensionality space.
798 However, unlike PCA, PLS seeks a projection that maximizes the correlation between each
799 component in the x space and the composition y. PLS handles data with a large number of
800 highly correlated independent variables well, and thus is commonly used with spectroscopic
801 data.

802 Support vector regression is based on the Support Vector Machine (SVM), in which data are
803 projected into a space where they can be effectively separated using a hyperplane [67,68]. For
804 regression, this hyperplane defines a region around the prediction within which errors are not
805 penalized. This allows the algorithm to focus on reducing the largest errors rather than making
806 insignificant improvements on predictions that are already close to the true value.

807 We used two ensemble methods as well: Gradient Boosting Regression (GBR; Friedman, 2002,
808 2001) and Random Forest (RF; Breiman, 2001), both of which are based on decision trees [72].
809 To build a decision tree, a series of binary splits (“branches”) are chosen. For regression trees,
810 it is common to choose a split that minimizes the variance. Once the decision tree is built, an
811 unknown spectrum begins at the tree “trunk,” and follows the set of branches, eventually arriving
812 at a “leaf”, which represents the prediction result. Decision trees have the disadvantage of
813 overfitting test data if the hierarchy is too deep. To prevent this overfitting, rather than using a
814 single decision tree, ensemble methods form predictions from a combination of multiple decision
815 trees. See [72] for more details on decision trees.

816 In RF regression [71], a set of decision trees is created by training on random subsets of the
817 training set and using random subsets of the input variables (spectral channels) as well. Taking
818 the average of a larger number of randomized decision trees generally causes their individual
819 errors to balance out, yielding an accurate regression model without suffering from overfitting.

820 GBR [69,70], on the other hand, is a technique for repeatedly adding decision trees so that the
821 next decision tree corrects errors in the prediction from the previous decision tree. This is done
822 using “boosting” [73] which is a technique that aggregates models developed sequentially on a
823 given learning task, with the weights assigned to the input data adjusted as new models are
824 added. At each step of the process, a new model is added and fit to the negative gradient of a

825 loss function. The loss function can be the mean squared error (MSE) which is not robust to
826 outliers, the mean absolute error (MAE) which is robust to outliers, or the Huber loss function
827 which transitions from MAE to MSE at a specified threshold [74].

828 As discussed above, one of the main challenges in developing a regression model for predicting
829 the composition of geologic materials on Mars is the wide range of potential compositions.
830 Models trained on a restricted range of compositions tend to perform well within that range, but
831 very poorly outside the training range. Models trained on a diverse set of samples, on the other
832 hand, tend to perform better overall, but within a specific range a specialized model may still do
833 better. For the calibration of the ChemCam instrument, we developed a “submodel” approach to
834 make use of this behavior [65]. By training several models on restricted ranges of composition,
835 and then using a single overarching model as a “first guess” to determine which submodel is
836 most appropriate for a given prediction, we can often improve the overall accuracy. The
837 disadvantage of the submodel approach is that it is relatively involved, requiring the cross
838 validation of several models, optimization of the blending of multiple models, and trial and error
839 to determine which algorithms and which training set ranges give the best results.

840 Local ENet is an algorithm that we developed as an alternative to the relatively involved process
841 of using blended submodels. It generates a new elastic net model for each unknown spectrum
842 being predicted, using the N most similar spectra in the training set, where N is a user-specified
843 number of nearest neighbors. The individual models are optimized using the automatic cross
844 validation capabilities of the implementation of Elastic Net in scikit-learn. Local Elastic Net is
845 inspired by the LOCAL algorithm [75], in which a weighted average of PLS models is used in a
846 similar manner. Local Elastic Net regression is time consuming since it trains many individual
847 models, but it has the advantage that it can adapt the training set to be as similar as possible to
848 the unknown spectrum without the need for human involvement. Our implementation of Local
849 ENet is available as part of the Python Hyperspectral Analysis Tool ([https://github.com/USGS-
850 Astrogeology/PyHAT](https://github.com/USGS-Astrogeology/PyHAT)).

851 To investigate the behavior of regression models, it is useful to see which spectral channels
852 influence the model the most. For the linear models above (PLS, Ridge, LASSO, Enet, OMP)
853 we use the vector of regression coefficients w that is multiplied by each spectrum to yield a
854 predicted composition. These can be plotted as a function of wavelength much like a spectrum
855 to see which parts of the spectrum have a strong positive or negative correlation with the
856 prediction. Ensemble methods do not have a perfectly analogous vector, since they comprise
857 many decision tree models. Instead, the scikit-learn implementation of GBR and RF provides a
858 “feature importance” or “Gini importance” vector. This is a vector of values that indicates which
859 spectral channels had the greatest influence on the model, but it is not a vector of weights that
860 is multiplied by the spectrum to yield a prediction.

861 4.2. Model Selection

862 With such a large variety of regression algorithms, the process of selecting between the models
863 for each element is very important. As discussed above, we use cross validation on the training
864 set to optimize the parameters of each model to minimize the RMSECV. Once the parameters

865 are set, we use the optimized models to predict the test set. The Root Mean Squared Error of
866 Prediction (RMSEP) of those test set predictions is the primary basis on which the best model is
867 selected. Rather than using a single RMSEP, we subdivide the test set and calculate the
868 RMSEP for all test set data acquired at 3 m, and SCCTs observed at 3 , 1.545, and 4.25 m.

869 The primary metric we use to select a model is the RMSEP for the test set spectra at 3 meters
870 (the most typical distance at which targets will be analyzed on Mars). For each element, several
871 models typically had a better performance than other models evaluated (lower RMSEP). For
872 models with similar RMSEP for data obtained at 3 m, we next evaluated the RMSEP with SCCT
873 data obtained at 1.545 and 4.25 m. All models for all elements performed worse at 4.25 m,
874 suggesting that there may be a problem with that set of data. Although the poor performance at
875 4.25 m is not fully understood, we favored models that were more robust to the differences in
876 that data set. We also calculated the RMSEP for just the SCCTs at 3 m. This was not used as
877 the primary statistic for model selection because the calibration targets include several
878 “extreme” compositions, but if the 3 m overall RMSEP was similar for multiple models, the
879 model with better performance on the calibration targets was preferred. Based on these
880 RMSEPs and other considerations such as model performance at low and high concentrations,
881 we identified several candidate regression models for each element for more detailed
882 evaluation.

883 The model selection steps described above were completed prior to landing on Mars. Once
884 initial spectra of calibration targets and geologic targets from the surface of Mars were available,
885 we began an additional stage of evaluation using those data. The calibration targets are useful
886 because they have a known composition; however, they are analyzed at closer distance than
887 the Mars target and a lower power must be used to prevent saturation. Mars geologic targets
888 are of unknown composition but can still serve as a valuable check to ensure that the
889 predictions are geochemically reasonable and are consistent with comparable spectra of known
890 composition from the laboratory. Depending on the grain size of minerals in a rock, the LIBS
891 analytical footprint may be small enough to analyze individual grains and return a pure mineral
892 composition. Observations that appear to be pure minerals or simple mixtures of minerals are
893 useful for evaluating model performance, because there are known geochemical constraints on
894 mineral compositions.

895 In April 2021, roughly two months after landing on Mars, the initial results were used in
896 conjunction with laboratory results to select a preferred model for each of the major elements
897 from among the candidates identified prior to landing. After that initial selection, we continued to
898 monitor the predicted compositions as additional targets were observed over the following
899 months. In September 2021, we reviewed the results from Mars and in several cases switched
900 to a different model based on our findings. We discuss this in more detail below for each
901 individual major element.

902 The test set predictions of the final selected models are shown in Figure 12, the SCCT
903 predictions on Mars are shown in Figure 13, and histograms of the compositions predicted for
904 Mars targets through Sol 239 are shown in Figure 14.

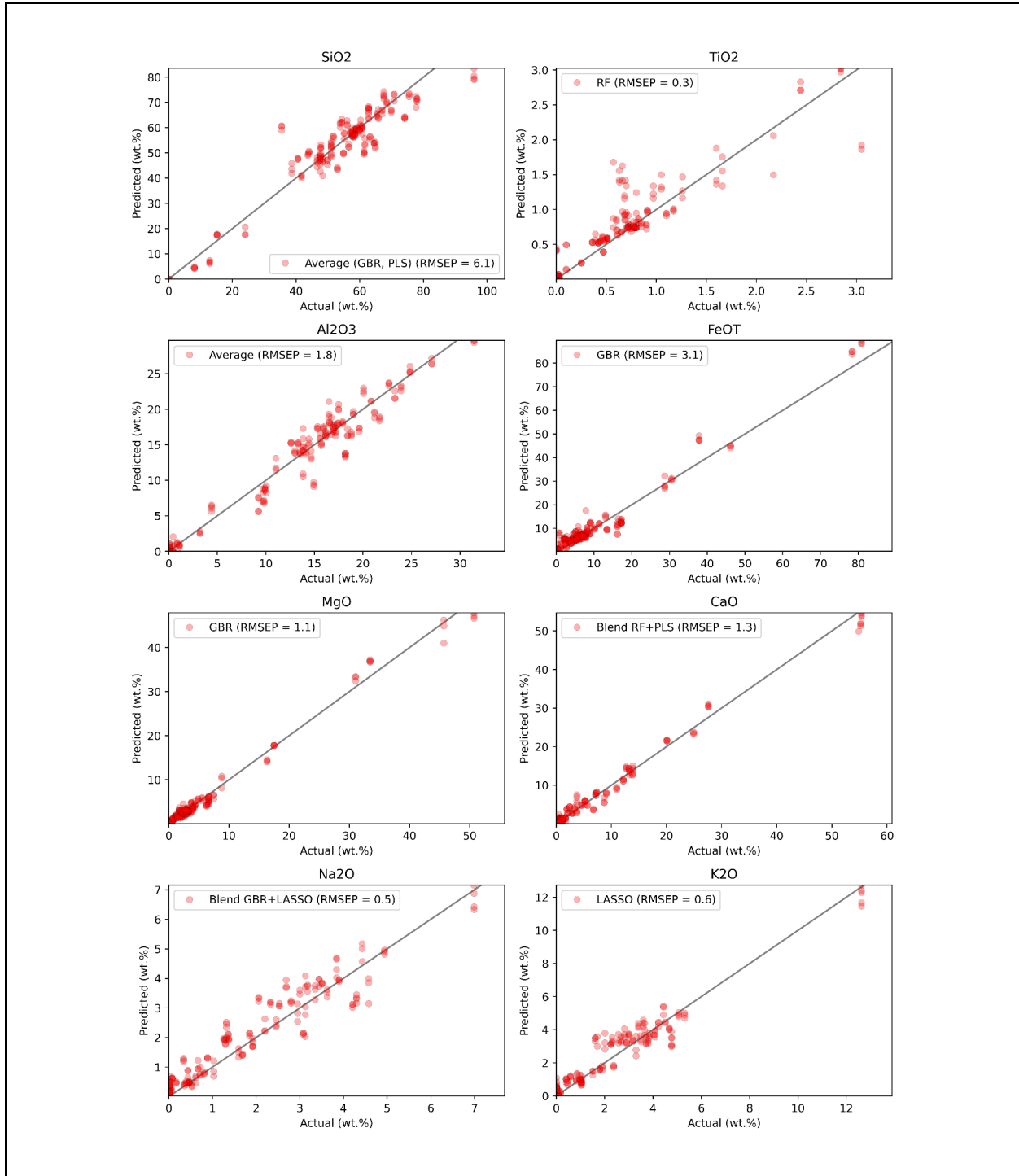


Figure 12: Test set predictions for each major element for the current selected models. Negative predictions are set to zero. Perfect predictions would fall on the diagonal (1:1) line. RMSEP indicates the overall accuracy in wt.% of the model when predicting the test set. SiO₂ results are the average of GBR and PLS predictions. Al₂O₃ results are the average of predictions using several different algorithms. CaO and Na₂O results use a blend of two

models to obtain more accurate results at both low and high concentrations (see text for details).

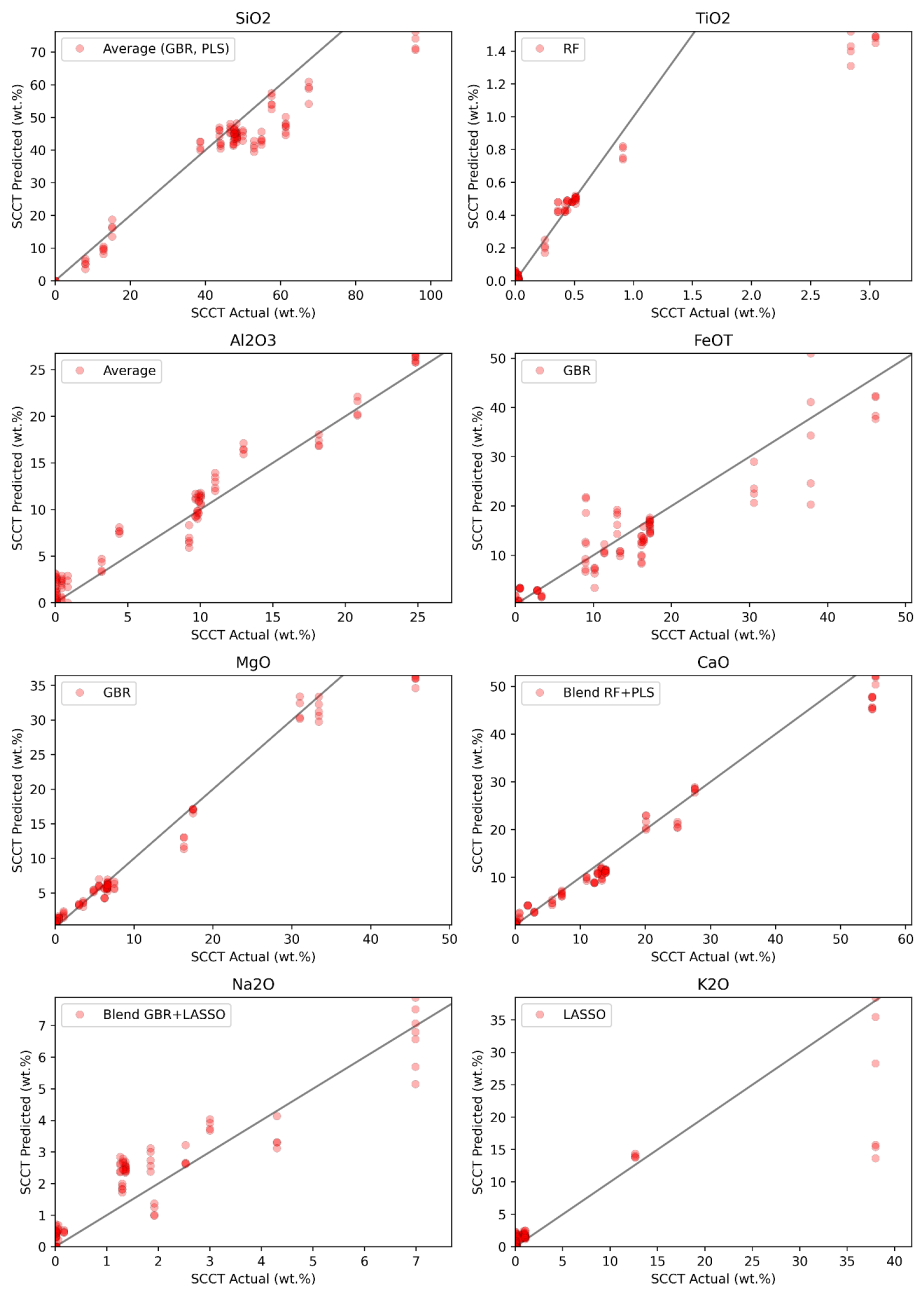


Figure 13: Prediction results for the SCCTs measured on the martian surface using the current selected models

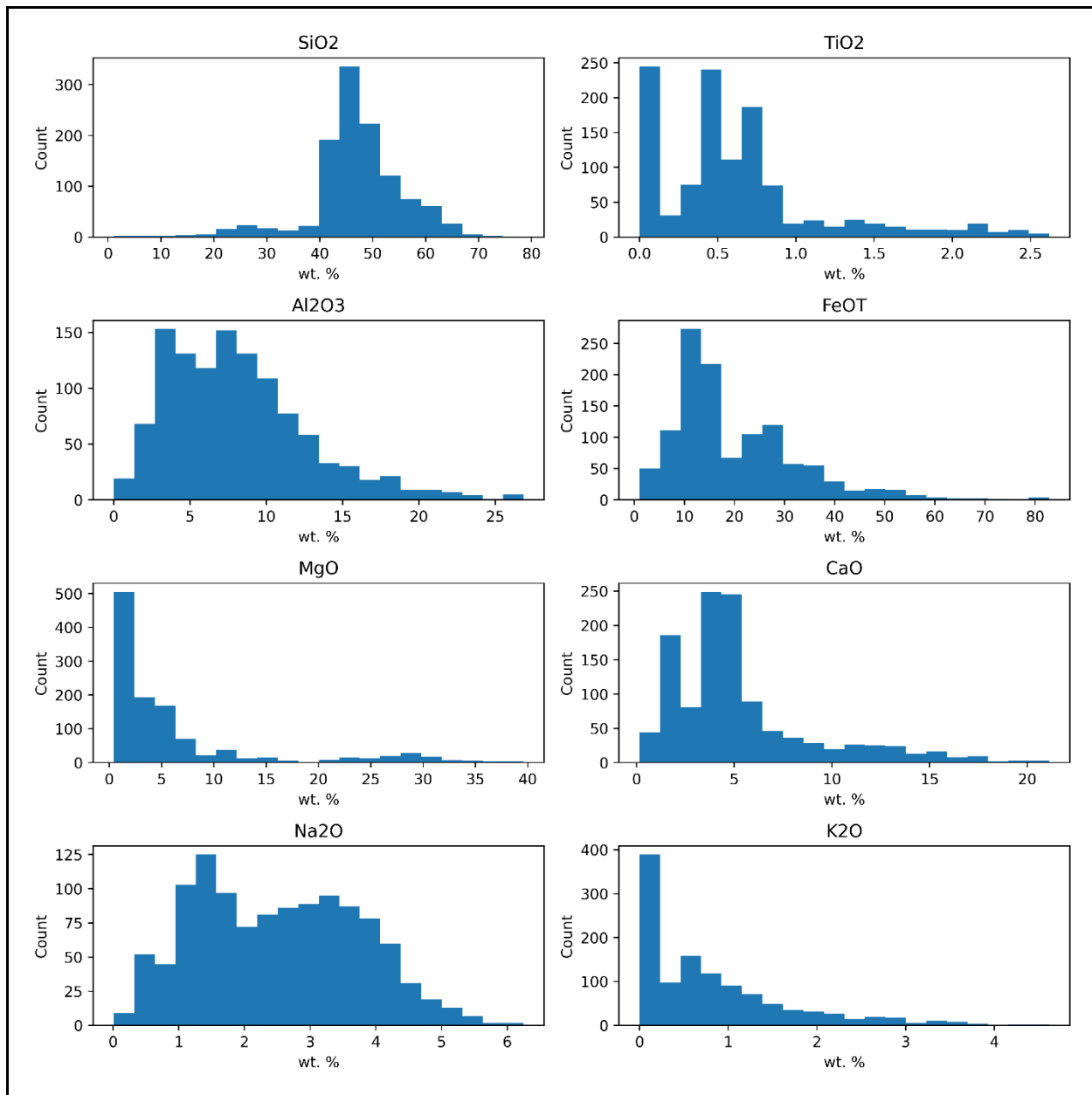


Figure 14: Histograms of predicted compositions of Mars geologic targets through Sol 239 for the selected major element models.

906

4.2.1. SiO₂

907 SiO₂ is a critical element for understanding both igneous and sedimentary geochemistry.
 908 In Gale crater, ChemCam analyzed targets with a wide range of predicted SiO₂ values from
 909 nearly 0 to >70 weight % [32,76]. Therefore, accurate predictions across a wide range of SiO₂
 910 values are critical for SuperCam as well.

911 Of the models considered for SiO₂, five had lower RMSEPs at 3 m and were investigated
 912 in more detail: RF, GBR, PLS, Local Elastic Net, and a blend of SVR, Elastic Net, and PLS

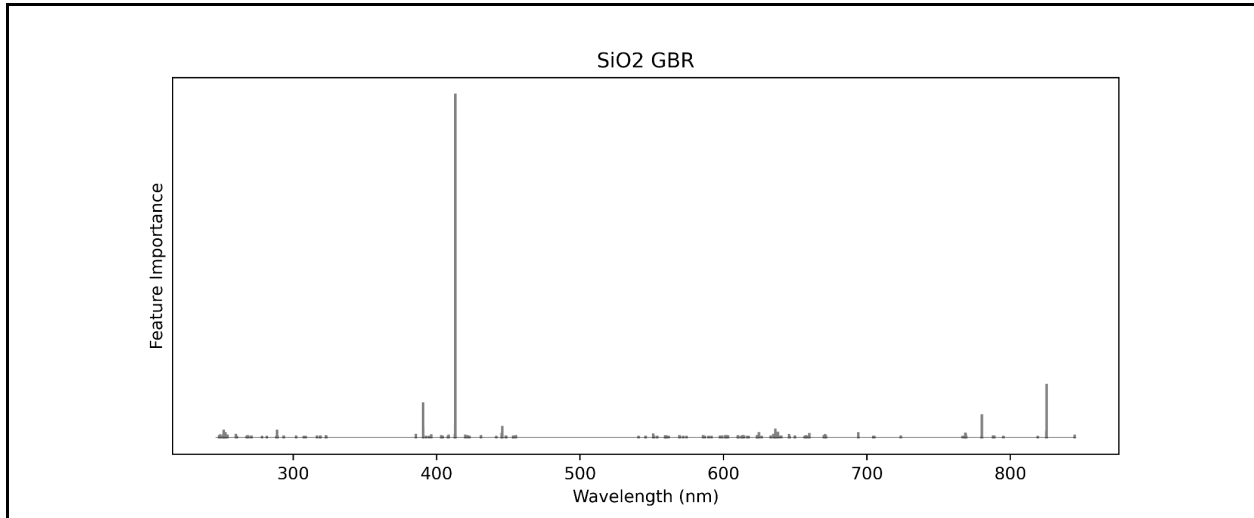
913 submodels. The blended model performed considerably worse on the 4.25 m data than the
914 other models and performed poorly at compositions >75 wt.%, so it was removed from
915 consideration. PLS had the best performance on the 4.25 m data, but GBR had a lower RMSEP
916 on the 3 m data, so an average of the GBR and PLS predictions was used to mitigate the errors
917 of the individual models (Figure 12). Figure 15 shows the feature importance values for the GBR
918 model and the regression coefficients for the PLS model.

919 The most important feature for the GBR model is the 413.04 nm spectral channel,
920 corresponding to the Si II lines at 412.9 nm and 413.2 nm. The PLS model does not show a
921 single dominant spectral channel. This PLS model uses standardized spectra, which results in a
922 more even spread of influence across the full spectrum.

923 Figure 13 shows results from the SCCT data collected on Mars. The low compositional
924 range is predicted accurately while the higher end tends to underpredict. The mid-range, from
925 ~38-60 wt.%, shows similar predicted values with considerable scatter, indicating poor
926 discrimination among these targets for SiO₂. This behavior is also observed in the other
927 regression models considered; it is not unique to the GBR and PLS models.

928
929 Figure 14 shows a histogram of SiO₂ predictions on Mars, excluding SCCTs, through sol
930 239. The majority of martian targets fall between ~40 and 65 wt.%, with a small number of
931 points exceeding 65 wt.%, and a significant number of predictions in the 0-40 wt.% range, likely
932 indicating mixtures between silicate and non-silicate minerals such as Fe oxides. In
933 investigation of LIBS points on possible pyroxenes, we find that the predicted SiO₂ content is 5-
934 10 wt.% lower than that of typical martian meteorites.

935



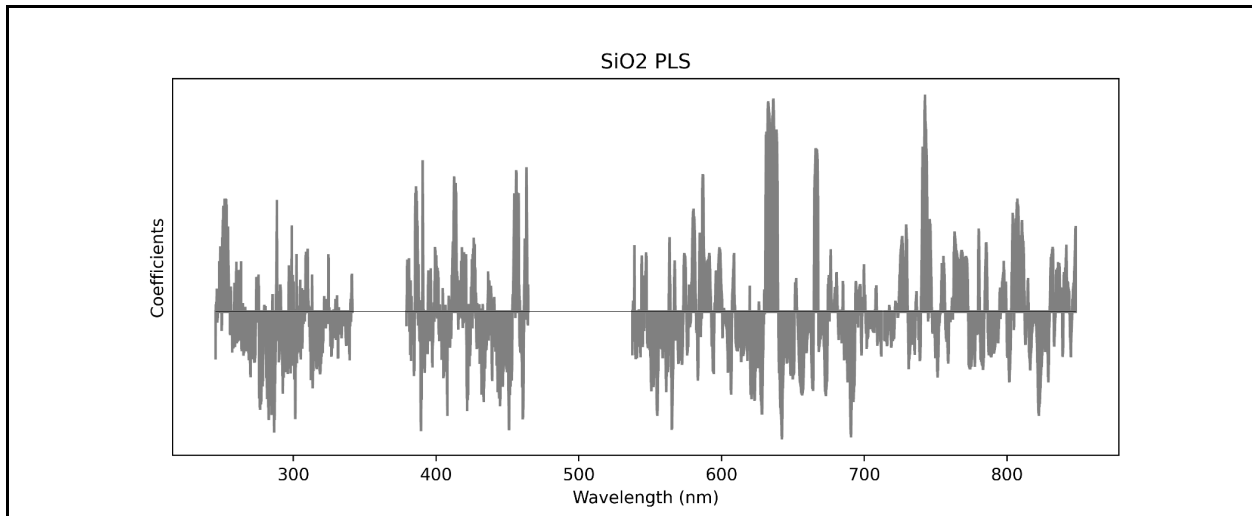


Figure 15: (top) Feature importance values for the SiO₂ GBR model. The most important feature is at 413.04 nm, corresponding to the Si II lines at 412.9 nm and 413.2 nm. (bottom) Regression coefficients for the SiO₂ PLS model. This model uses standardized spectra, so individual strong lines are less favored, and the influence on the model is more evenly spread across the spectrum.

936

937

4.2.2. TiO₂

938 The choice of regression model for TiO₂ was relatively straightforward: the models with the best
 939 performance at 3 m were GBR, RF, and a blend of elastic net submodels, all with an RMSEP of
 940 ~0.3 wt.%. Of these models, RF exhibited better performance at 4.25 m, and was therefore
 941 selected. Figure 12 shows the performance on the laboratory test set. The scatter in the
 942 predictions is smaller at the low end and increases toward higher concentrations. A group of
 943 samples at ~0.6 wt.% actual TiO₂ content are overpredicted and are visually notable in the plots,
 944 but most samples with compositions <1 wt.% TiO₂ are predicted accurately. Figure 16 shows
 945 the feature importance values for the RF model. This model uses a different mask than other
 946 models discussed in this paper. It was trained on spectra with the full transmission spectrometer
 947 masked out and thus relies strictly on the UV and VIO spectrometers. The most important
 948 spectral channels (Figure 16) correspond to several Ti II lines in the UV.

949

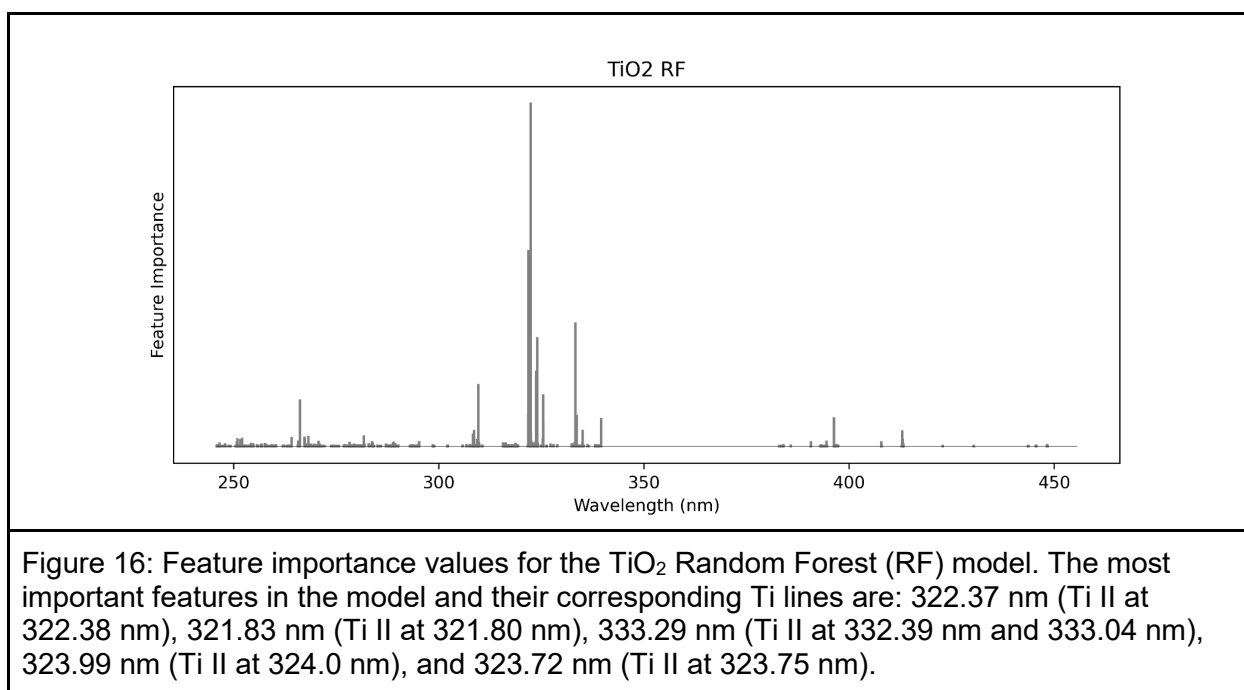
950 Figure 13 shows the TiO₂ predictions on the SCCTs on Mars. The TiO₂ model performs well on
 951 SCCTs with TiO₂ <1 wt.%, but predicts a range of 1.3 wt.% - 1.5 wt.% for LBHVO2 (actual TiO₂
 952 wt.% of 2.84 wt.%). This target is predicted accurately in the laboratory data. The other high
 953 TiO₂ SCCT (LJSC1; actual TiO₂ of 3.05 wt.%) is underpredicted in both the laboratory and on
 954 Mars.

955

956 In martian data, several observations for which the RF model predicts compositions between 2
 957 and 3 wt.% have LIBS spectra that suggest a far greater TiO₂ content, more similar to the
 958 laboratory spectra of ilmenite. These points highlight a limitation of the ensemble methods such
 959 as RF and GBR. Whereas methods such as LASSO or PLS may underpredict samples with

960 very high concentration, they are capable of some degree of extrapolation and can yield
961 predicted compositions outside of the training set used for the model. RF and GBR, on the other
962 hand, do not predict values outside of the range of compositions in their training set. The
963 training set used for TiO₂ has a maximum value of 3.4 wt.%, and therefore no higher TiO₂
964 predictions are possible from the RF model. Two samples in the laboratory database did have
965 higher TiO₂ concentrations but were excluded from modeling because they were too spectrally
966 distinct. One is pure ilmenite (36 wt.% TiO₂) and one is a mixture of basalt and ilmenite (6.6
967 wt.% TiO₂). We experimented with a RF model that incorporated these higher TiO₂ samples in
968 the training set, and it did yield much higher TiO₂ predictions on the Mars spectra in question,
969 but at the expense of degraded performance on low-TiO₂ samples. It was also impossible to
970 evaluate the accuracy of this high TiO₂ model for high-concentration (>5 wt.%) targets, since the
971 only high-TiO₂ samples were used to train it, and the Mars sample compositions are unknown.
972 Since most geologic targets are low in TiO₂ (<2 wt.%), we chose to continue to use the original
973 RF model and flag spectra that predict near the upper end of the training set range as requiring
974 special attention.

975
976



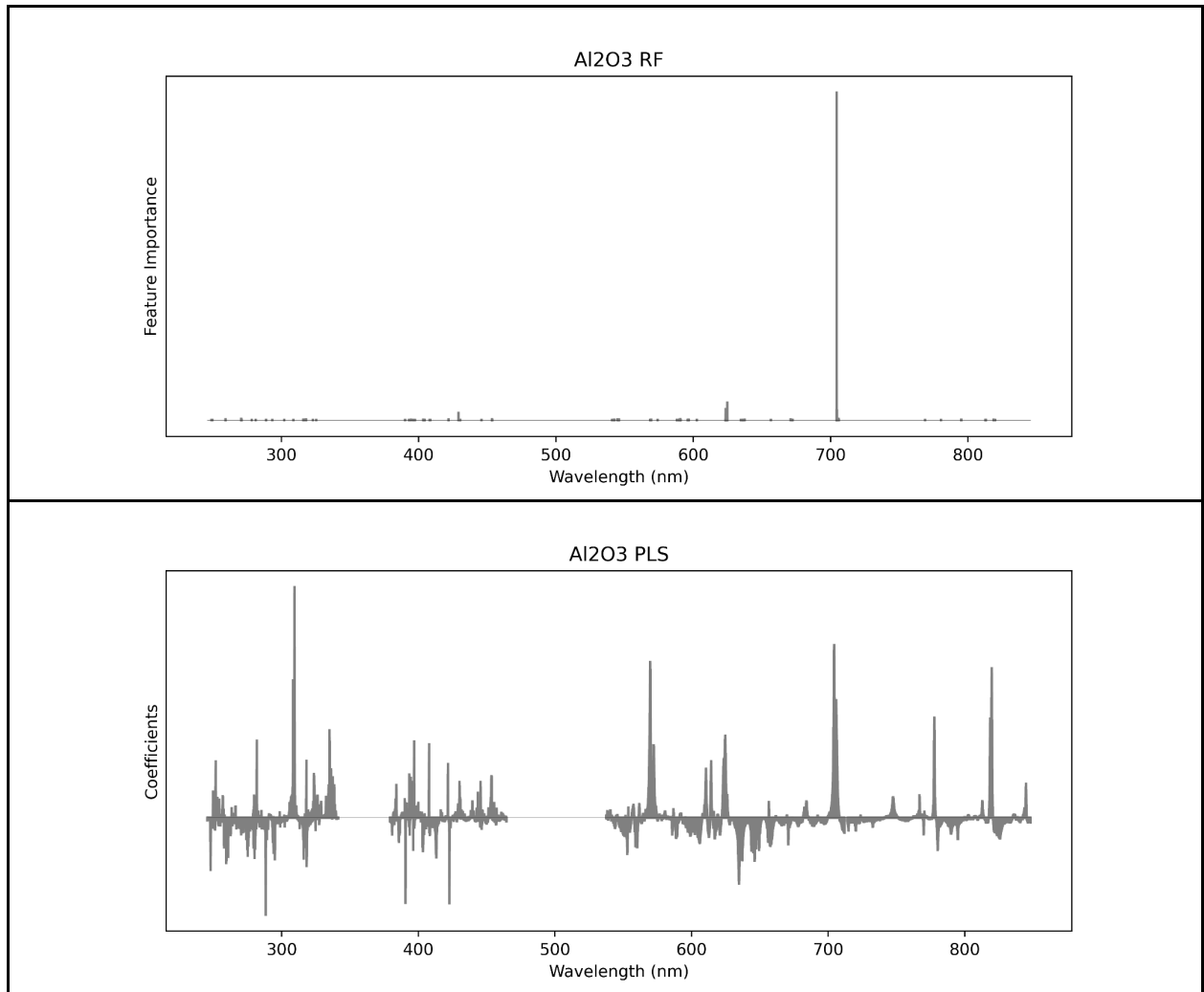
977

978 4.2.3. Al₂O₃

979 For Al₂O₃, the four models investigated in detail were Local ENet, RF, and two variants of PLS;
980 one with peak binning and standardization and one without. Local ENet had the lowest 3 m
981 RMSEP (1.97 wt.%), but we found that an average of the predictions from these four models
982 resulted in a lower 3 m RMSEP than any of the individual models (1.8 wt.%), so the average
983 was chosen as the preferred “model.” Figure 12 shows that the test set predictions perform well
984 across the range of compositions, although moderate concentrations (10-20 wt.%) exhibit more

985 scatter in the predictions than either the low or high ends. Figure 17 shows the feature
986 importance values for the RF model and the regression coefficients for the two PLS models.

987



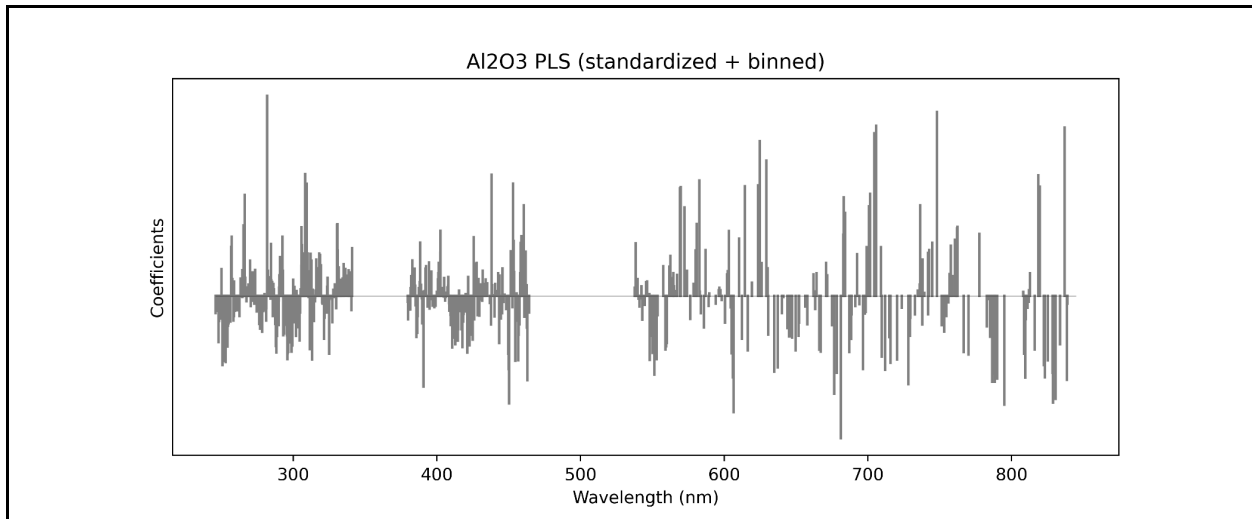


Figure 17: Feature importance values and regression coefficients for three of the four models that are averaged for the Al_2O_3 predictions. The Local ENet model does not have a fixed set of coefficients, since the local model trains on the fly based on the unknown spectrum. (top) The RF model relies almost solely on the spectral channel at 704.38 nm corresponding to the Al II line at 704.4 nm. (middle) PLS using 11 components, without peak binning or standardization applied. Strongest coefficients correspond to the following lines: Al I at 309.37 nm, Al II at 704.4 nm, Na I 568.98 nm, Na I 819.71 nm. There are notable negative coefficients at 288.24 nm (Si I), 390.67 nm (Si I at 390.66 nm), and 422.8 nm (Fe I at 422.86 nm or Ca I at 422.79 nm). (bottom) PLS using 13 components on peak binned, standardized spectra. The five strongest coefficients are at 281.75 nm (Al II at 281.7 nm), 748.05 nm (O I at 748.24 nm), 705.89 nm (Al II at 705.86 nm), 837.01 nm (Al II at 836.58 nm), and 704.38 nm (Al II at 704.4 nm), although standardization results in numerous other strong coefficients.

988 The Al_2O_3 model performs well on the Mars SCCTs, with most predictions close to the true
 989 composition (Figure 13). Of particular interest are the SCCTs PMIAN (andesine; 24.84 wt.%
 990 Al_2O_3), LJSC1 (JSC Mars-1 simulant; 20.83 wt.% Al_2O_3), and PMIOR (orthoclase; 18.18 wt.%
 991 Al_2O_3). These targets are accurately predicted by the Al_2O_3 model, indicating that the model
 992 performs well on feldspars. Figure 14 shows the distribution of Al_2O_3 predictions on Mars. Most
 993 targets have <10 wt.% Al_2O_3 , but a significant “tail” of predictions extends up to ~27 wt.%.

994 Based on Mars surface data gathered so far at Jezero crater, restricted to samples with
 995 concentrations of SiO_2 (>35%), Al_2O_3 (>10%), Na_2O (<20%) and CaO (<30%) compatible with
 996 feldspars, no target has sufficient K_2O to be clearly identified as K-rich feldspar. However, there
 997 are many candidates with compositions similar to those calculated for the Andesine and JSC
 998 Mars-1 SCCTs (Figure 18). Plagioclases are the dominant feldspars detected by CheMin at
 999 Gale crater [77], with the exception of the Windjana location which contained K-rich feldspar
 1000 [78].

1001

1002

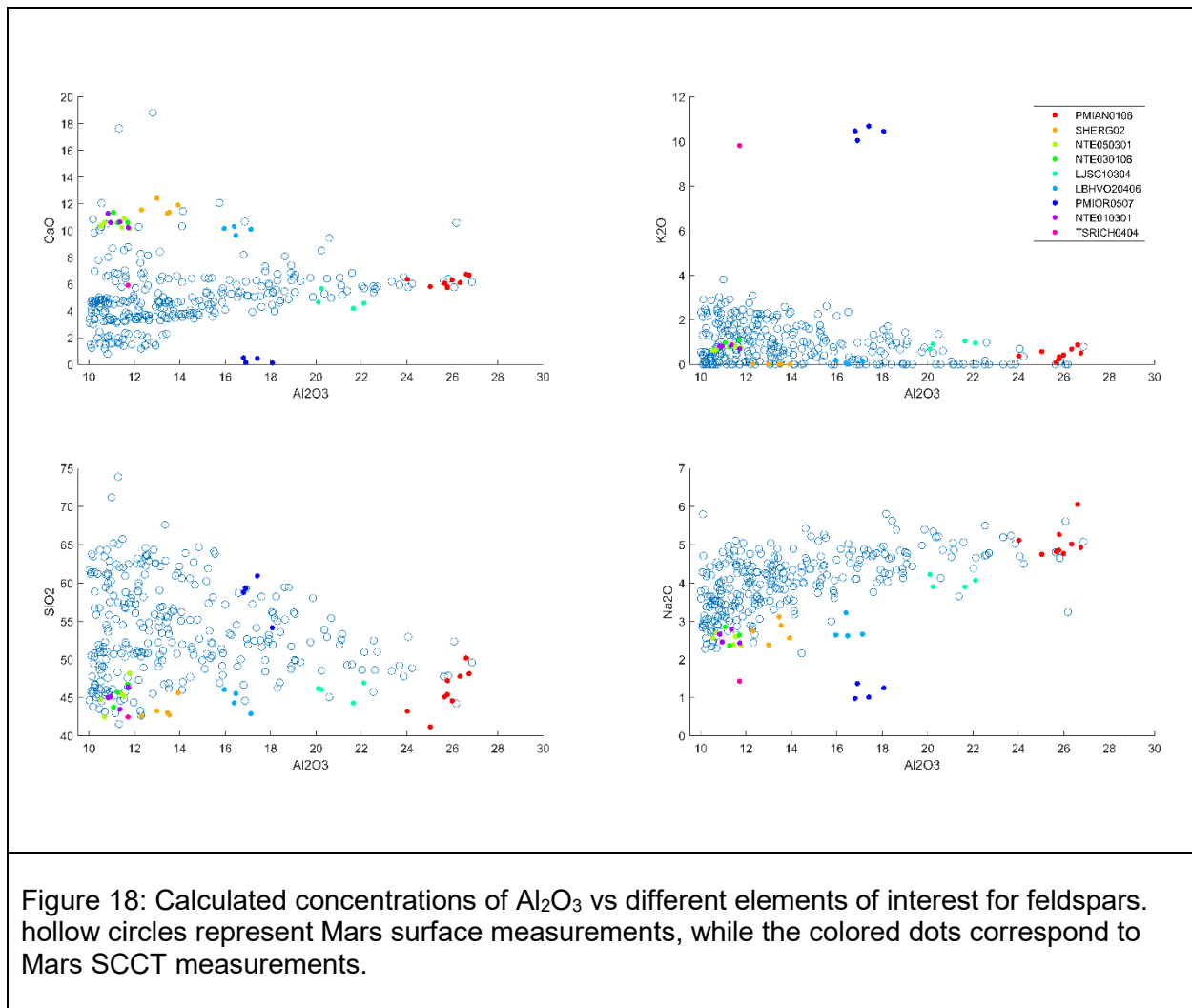


Figure 18: Calculated concentrations of Al_2O_3 vs different elements of interest for feldspars. hollow circles represent Mars surface measurements, while the colored dots correspond to Mars SCCT measurements.

1003 We observe some evidence that spectra from targets with high TiO_2 concentrations may result
 1004 in overestimates of Al_2O_3 . This is likely due to the large number of emission lines present in the
 1005 spectra of high- TiO_2 samples, which overlap with positive loadings in the Al_2O_3 models. For
 1006 example, consider the surface target Ha'íí'áąągo (Haa_ii_aah¹) Point 1 on this target has a very
 1007 high concentration of TiO_2 (predicted as 2.6 wt.% but likely significantly higher) and the Al_2O_3
 1008 model predicts a concentration of 17.4 wt.%. The spectra from this point have weak Al lines, but
 1009 numerous Ti lines. Table 4 compares the predictions from each Al_2O_3 model for this target. The
 1010 RF model predicts a much lower concentration (4.8 wt.% Al_2O_3), which is more similar to the
 1011 composition of other points on the target. The features with higher weight in RF calculations are
 1012 mainly located at 704 nm (Figure 17). Ti has many emission lines, particularly in the UV range,
 1013 so the reliance on a longer wavelength Al line may make the RF model less sensitive to high Ti.
 1014 The overall performance of the averaged models is more accurate than that of RF alone, so we

¹ Targets early in the mission were given names in the Navajo language because the rover landed in an area of the landing site named after Canyon de Chelly National Monument, which is within the Navajo Nation. For situations where special characters cannot be used, such as in commands sent to the rover, a "plain text" version of the name that approximates the pronunciation is used. We list both versions.

1015 still use the average as the default prediction. However, this illustrates that caution should be
 1016 used in cases with high Ti and that the RF model may be a viable alternative in such cases.

Table 4: TiO₂ and Al₂O₃ predictions in wt.% for target Ha'íí'áago (Haa_ii_aah)

Point	TiO ₂ Predictions	Al ₂ O ₃ Predictions				
		PLS (binned + standardized)	Local ENet	PLS	RF	Average
1	2.6	21.4	26.0	17.4	4.8	17.4
2	0.8	8.0	9.6	7.3	5.1	7.5
3	1.6	3.5	7.6	5.6	5.1	5.5
4	0.1	5.2	7.8	3.8	5.3	5.6
5	0.5	12.2	13.5	11.6	15.0	13.1
6	0.8	10.0	10.2	8.9	5.6	8.7
7	0.7	6.5	9.4	7.1	12.8	9.0
8	0.9	8.0	10.5	8.1	13.1	9.9
9	0.9	6.9	10.8	7.5	5.9	7.8
10	0.3	14.0	11.1	11.5	12.5	12.3

1017 **4.2.4. FeO_T**

1018 Selection of an FeO_T model was subject to considerable discussion. Of the models evaluated,
 1019 GBR and RF had the best performance at 3 m and at 4.25 m. The RF model was initially
 1020 selected as the preferred model, based on its performance at both high and low extremes of
 1021 composition in the test set. Preliminary Mars results seemed to support the selection of RF as
 1022 the preferred model. In particular, point 1 on the target Dii' (Dii_scam) and point 6 on the target
 1023 Tsé libá (Tselhbahih) both exhibited high FeO_T concentrations. Comparison with laboratory
 1024 spectra indicated that the RF model was likely closer to the true composition, while GBR was
 1025 likely overestimating FeO_T in Fe-rich targets.

1026
 1027 However, additional results from Mars have led us to revisit the decision to use the RF model
 1028 rather than the GBR model. In particular, in studying the results from candidate high-Ca
 1029 pyroxenes, the stoichiometry using RF indicated that the FeO_T content may be underestimated
 1030 by ~4 wt.%, and resulted in compositions that fell outside those permitted for pyroxenes.
 1031 Substituting the GBR FeO_T predictions for the RF predictions resulted in more realistic
 1032 stoichiometry overall, but also increased the overall scatter in the results. The effect of switching
 1033 from RF to GBR was evaluated on several other groups of targets as well. For points with MgO
 1034 content >20 wt.%, switching to GBR yields stoichiometries more consistent with olivines. For

1035 targets where the sum of the major elements is >110 wt.%, switching from RF to GBR brings the
1036 totals closer to 100 wt.%. For these reasons, we chose to switch to GBR as the preferred model
1037 for FeO_T. The results for the laboratory 3 m test set are shown in Figure 12, and the Mars SCCT
1038 results are shown in Figure 13. Figure 19 shows the feature importance values for the GBR
1039 model and indicates that the model results are primarily driven by Fe I and II lines in the UV and
1040 VIO spectrometers.

1041
1042 The distribution of the GBR FeO_T predictions for all Mars geologic targets to date (Figure 14)
1043 peaks at ~12-15 wt.%, with a long tail toward higher concentrations. In general, we find that the
1044 estimated FeO_T content of rocks and soils analyzed by *Perseverance* is lower than other sites
1045 on Mars. This is best illustrated by examining the results from the first LIBS shots on geologic
1046 targets, which are dominated by dust. Since martian dust is highly mobile and globally
1047 distributed, it is assumed to be homogeneous across different landing sites. Results from
1048 ChemCam at Gale crater give a dust FeO_T content of ~20 wt.% [79], similar to the estimated
1049 FeO_T content for dust rich soils (17 wt.%) and the average martian crust (18 wt.%). By contrast,
1050 all of the regression models considered for SuperCam tend to underpredict FeO_T abundance in
1051 the dust, giving results closer to 12 wt.%.

1052

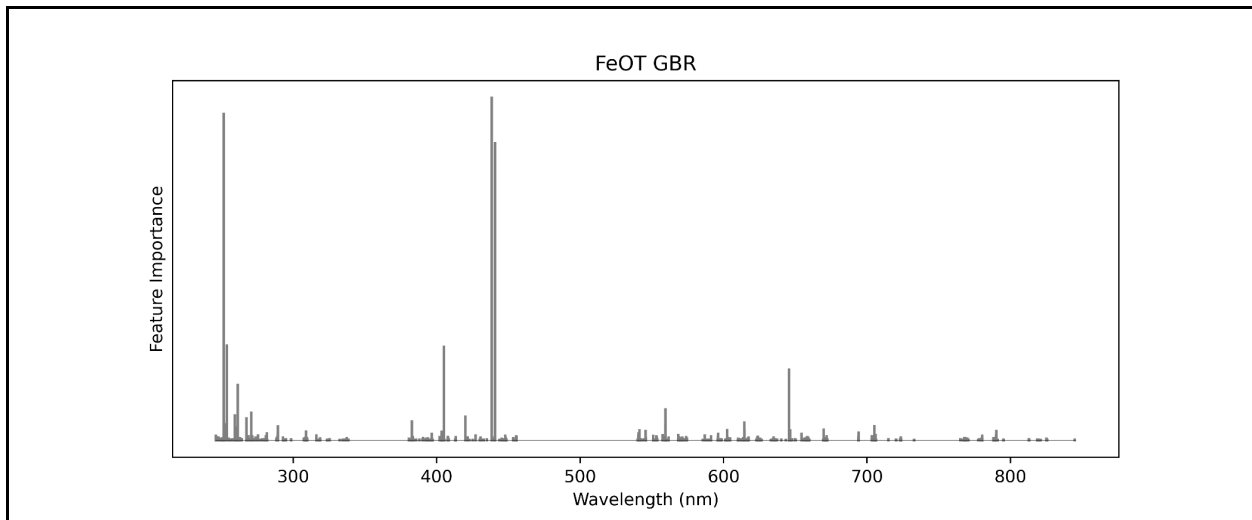


Figure 19: Feature importance values for the FeO_T GBR model. The most important features are at 438.46 nm (Fe I at 438.48 nm), 440.61 nm (Fe I at 440.6 nm), and 251.59 nm (Fe II at 251.51 nm).

1053

1054 4.2.5. MgO

1055 The four MgO models that were evaluated in detail were RF, GBR, ENet, and PLS, and they all
1056 performed well for the 3 m test set data. GBR had the lowest RMSEP (1.1 wt.%), closely followed
1057 by RF (1.22 wt.%). Both models also inherently avoid negative predictions, while the ENet and
1058 PLS models had some negative predictions for low-MgO targets. RF showed a slight tendency to
1059 overpredict MgO for high concentration samples, so GBR was selected as the preferred model.

1060 Figure 12 shows GBR results for the 3 m test set. The GBR model relies heavily on two spectral
1061 channels corresponding to the Mg II emission line at 448.238 nm (Figure 20).

1062 The GBR model performs well on most of the SCCTs in Mars data, as shown in Figure 13. The
1063 model underpredicts the diopside SCCT (PMIDN) both on Mars and in the laboratory data set
1064 (actual MgO content of 16.32 wt.%) but performs well on the ankerite SCCT (LANKE; actual MgO
1065 content of 17.46 wt.%). The most notable deviation is that GBR predicts values of 34.6-36.4 wt.%
1066 for the Serpentine/Talc SCCT (TSERP), when the actual MgO content is 45.68 wt.%. This
1067 underprediction is not observed in the laboratory results.

1068 In the LIBS data collected on Mars, the GBR model appears to be performing relatively well,
1069 predicting a wide range of composition from depleted to significantly Mg-rich rocks (Figure 14).
1070 There is no clear correlation with any other of the major elements except some clusters of points
1071 that may correspond to major mineral classes (e.g. olivines, pyroxenes). There is no noticeable
1072 relation between MgO prediction and distance to the target.

1073 One possible area of concern is that the points that are highest in MgO also tend to be the points
1074 with major element totals exceeding 100 wt.%. Some of these cases approach 130 wt.%, which
1075 is well beyond what can be explained by the RMSEPs for each element and suggests a systematic
1076 bias in one or more of the most abundant elements in the target (MgO, SiO₂, or FeO_T). A number
1077 of these points have LIBS spectra and estimated compositions consistent with olivine based on
1078 comparison with SCCT PMIFA on Mars, and the presence of olivine has been confirmed by
1079 SuperCam Raman spectroscopy. The stoichiometric ratios of FeO_T, MgO, and SiO₂ in the olivine-
1080 bearing points are consistent with olivine, but MgO is not particularly high for olivine (e.g.
1081 compared to PMIFA). The high totals may come from the contribution of other elements rather
1082 than an overestimate of MgO. Note that predictions for the analysis of SCCT PMIFA on Mars do
1083 not show a high total.

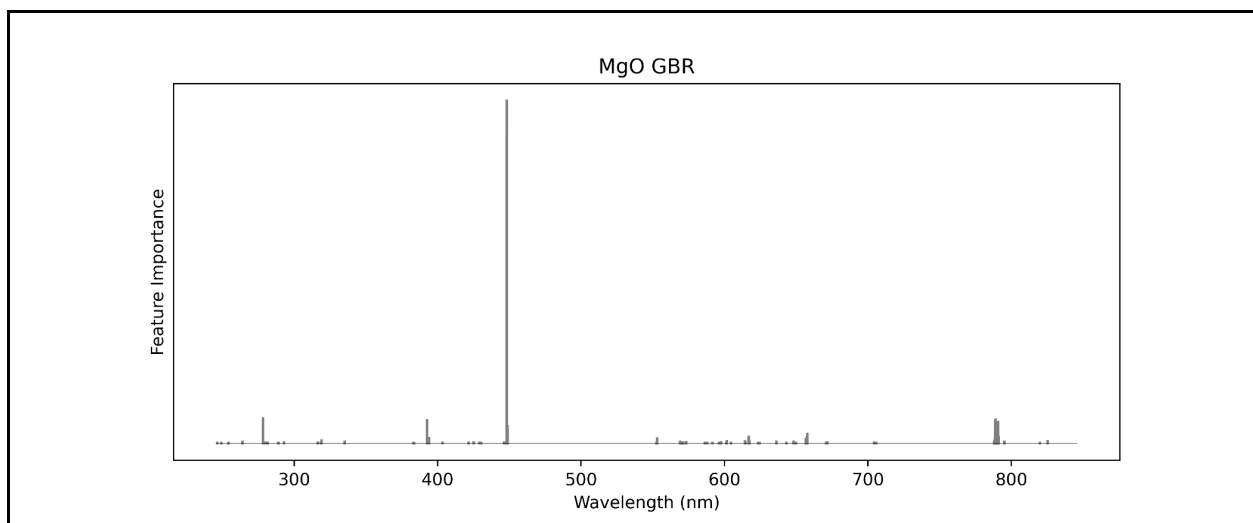


Figure 20: Feature importance values for the MgO Gradient Boosting Regression (GBR) model. The most important features are at 448.21 and 448.24 nm (Mg II at 448.238 nm).

1084

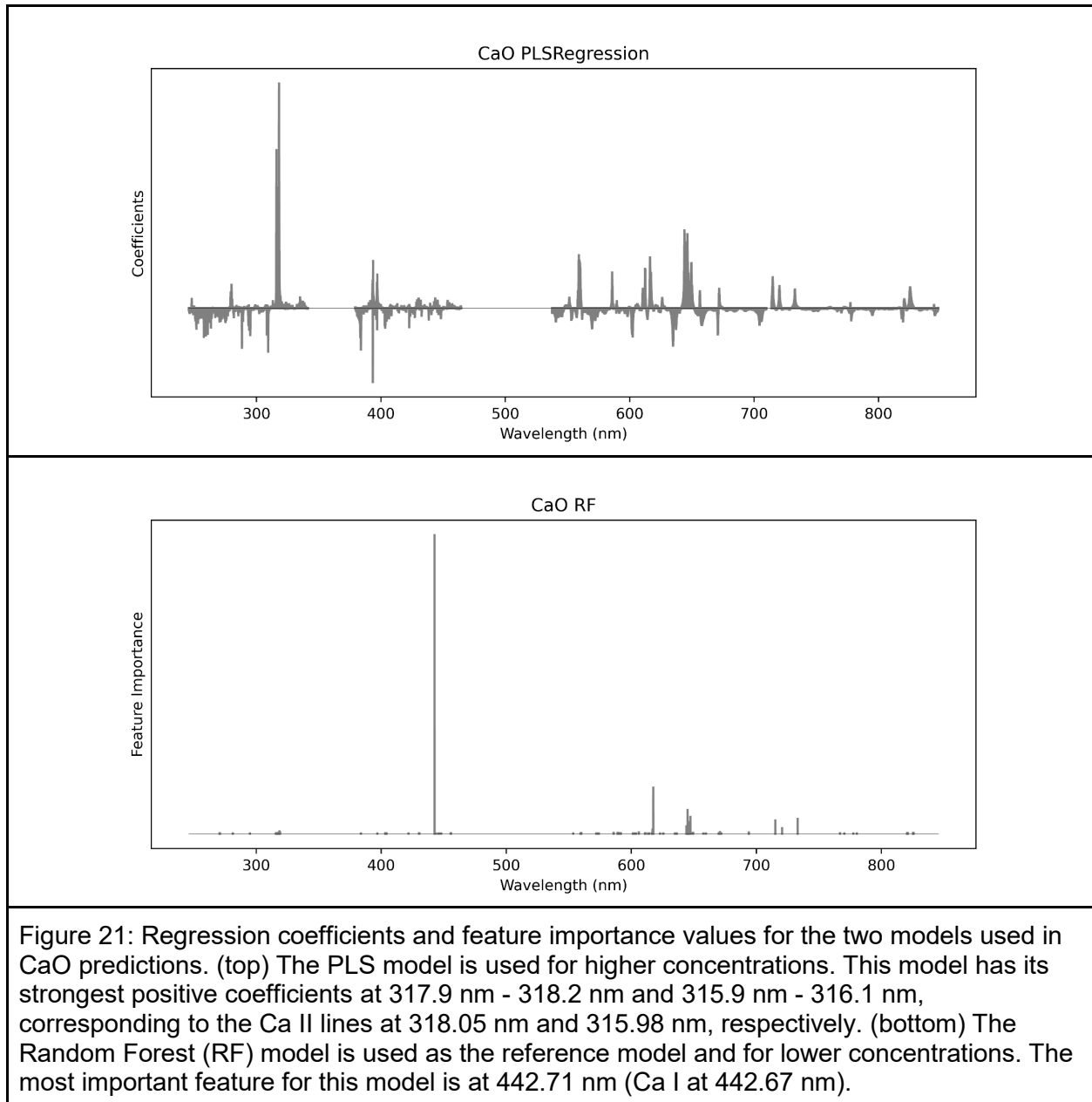
4.2.6. CaO

1085 The five best models for CaO calibration were RF, Elastic Net, SVR, and two instances of PLS
1086 (with and without peak binning). The RF model yielded the lowest 3 m RMSEP (1.51 wt.%) and
1087 was the only algorithm that produced universally positive predictions; all other tested models
1088 predicted negative CaO values for some low-CaO samples. Consequently, the RF model was
1089 selected as the preferred model for CaO.

1090 However, martian surface measurements indicated that the RF model was not performing as
1091 well as expected. The CaO predictions showed a bimodal distribution, with most predictions
1092 falling in one of two clusters centered around 6 and 20 wt.%, respectively. This bimodal
1093 distribution is not reflected in the Ca emission line intensities in normalized spectra, which are
1094 more evenly distributed. Likewise, the bimodal distribution predicted by the RF model is not
1095 reflected in any of the other candidate models, suggesting that the observed data structure is
1096 intrinsic to the RF algorithm and is not representative of the true distribution of CaO at Jezero
1097 crater.

1098 In response to this behavior on martian data, we evaluated the average of the two best models:
1099 RF and PLS without peak binning. This reduced but did not eliminate the bimodal behavior, and
1100 introduced numerous negative predictions at low concentrations due to the PLS model.
1101 However, the PLS model alone showed better results for higher concentrations and lacked the
1102 spurious bimodal behavior. This led us to use a blended submodel approach, with the RF model
1103 used as both the “reference” model and the “low” model, and the PLS model used for cases in
1104 which the reference model predicts high concentrations of CaO. The range over which the two
1105 models are blended was optimized based on the training set, resulting in the following values:
1106 For RF predictions <4.33 wt.%, the results are used without any modification. For RF
1107 predictions between 4.33 wt.% and 8.9 wt.% the RF and PLS predictions are combined in a
1108 weighted sum, with the weights determined by where in the range the initial RF prediction falls.
1109 For RF predictions >8.9 wt.% the PLS prediction is used instead. The result has a RMSEP on
1110 the 3 m test set of 1.3 wt.% (Figure 12), and performs well on the Mars SCCT data (Figure 13).
1111 The regression coefficients for the PLS model (Figure 21) show a strong positive weight on
1112 several Ca emission lines, and the RF model feature importance highlights the Ca I 442.67 nm
1113 line.

1114 The histogram of CaO predictions for Mars geologic targets (Figure 14) shows that the group of
1115 predictions at ~20 wt.% is no longer evident, though there is still some degree of bimodality in
1116 the lower CaO results, with groups of predictions at ~2 wt.% and at 4-5 wt.%. Preliminary
1117 attempts to correct for this behavior suggest that models based on just the UV and VIO
1118 spectrometers produce a smoother CaO distribution, and work is ongoing to evaluate these
1119 results.



1120

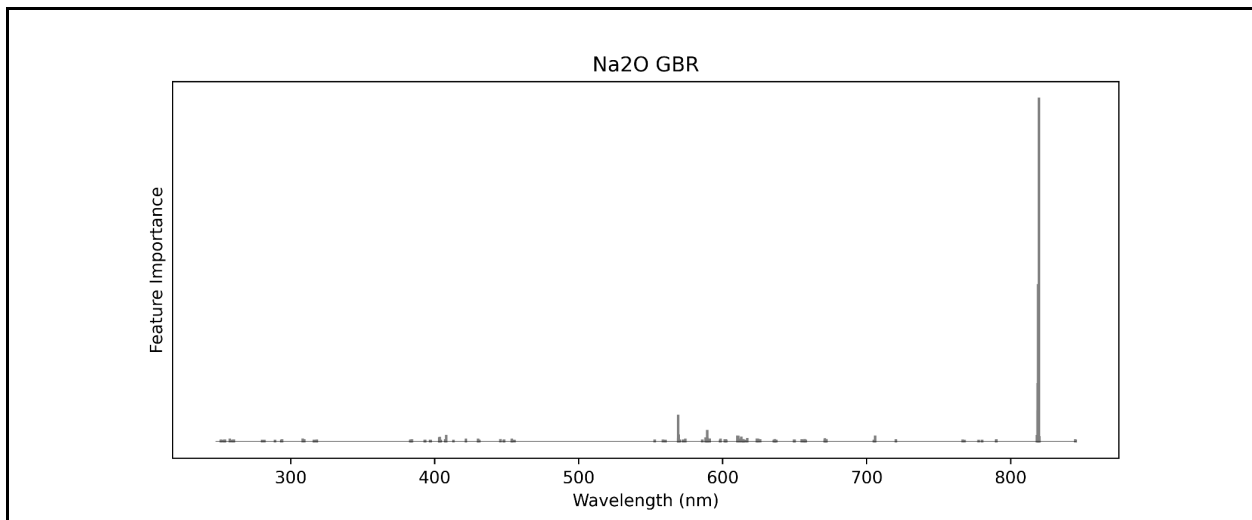
4.2.7. Na₂O

1121 For Na₂O, four models had a similarly low 3 m test set RMSEP (between 0.5 and 0.6 wt.%):
 1122 LASSO, GBR, and two different Blend models, referred to as “Blend A” and “Blend B.” To
 1123 choose among these models, we compared their predictions on initial Mars data. The Blend A
 1124 and Blend B model had similar results, with their highest predictions reaching ~4.5 wt. %. In
 1125 contrast, GBR and LASSO had predictions >5.5 wt. %. By comparing the LIBS spectra of the
 1126 points with the highest Na₂O predictions with laboratory spectra, we determined that the Na₂O
 1127 content seemed to be underestimated with the Blend A and B models, so those models were
 1128 eliminated from consideration.

1129 We next investigated the differences between the GBR and LASSO. We initially picked
1130 GBR; however, we found that some Mars data were trending towards plagioclase composition
1131 in terms of each major element, except for Na₂O, which appeared to be underestimated. We
1132 found that LASSO predicted higher values (up to 7.5 wt.%) compared to GBR (up to 6 wt.%).
1133 This behavior was confirmed by evaluating the GBR and LASSO predictions of the andesine
1134 SCCT: LASSO predicts the Na₂O in andesine more accurately than GBR. The disadvantage of
1135 the LASSO model was that it gave a large number of negative values on observations with low
1136 Na₂O.

1137 To combine the better performance of the GBR model at low concentrations with the
1138 better performance of LASSO at high concentrations, we developed a blended model that uses
1139 GBR as the “reference” model and at the low end (when GBR predicts Na₂O <3.335 wt. %), a
1140 weighted sum of GBR and LASSO between 3.335 wt.% and 5.458 wt.%, and LASSO only when
1141 GBR predicts Na₂O > 5.458 wt. %. These blending ranges were optimized on the training set.
1142 See [65] for details of the submodel blending process.

1143 The performance of this blended model on the 3 m test set is shown in Figure 12
1144 (RMSEP of 0.5 wt.%), and the Mars SCCT performance is shown in Figure 13. The feature
1145 importance values and regression coefficients for the GBR and LASSO models (Figure 22)
1146 show that the GBR model relies heavily on the Na I lines at 819.704 nm and 819.708 nm. The
1147 LASSO model uses several Na emission lines, but also uses negative coefficients
1148 corresponding to Ca. Figure 14 shows the distribution of Na₂O predictions for Mars geologic
1149 targets.
1150



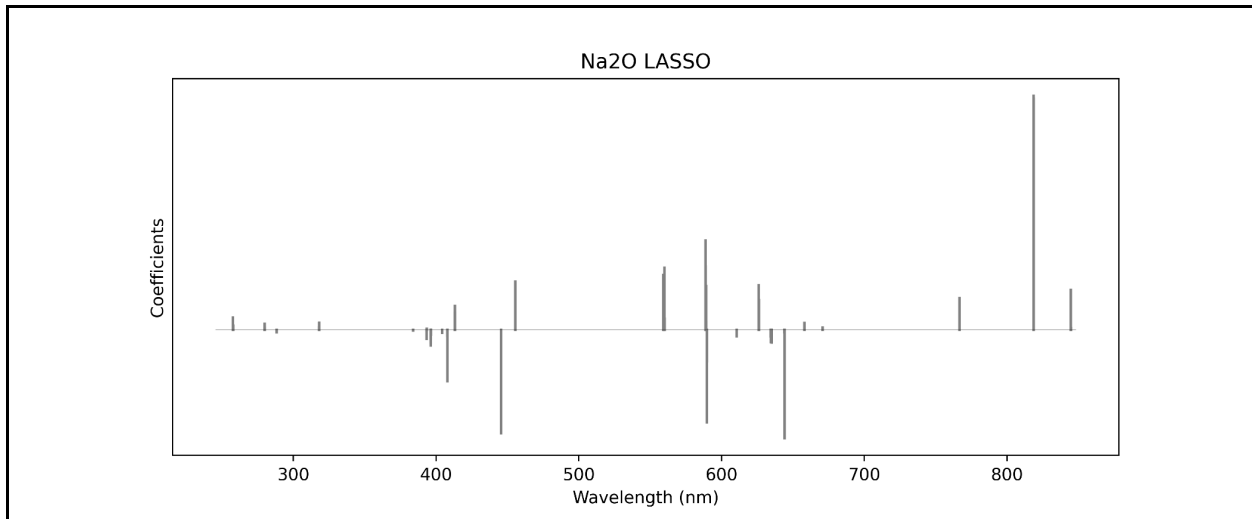


Figure 22: Feature importance and model coefficients for the two models used in the Na₂O predictions. (top) The GBR model is used as the reference model and for predictions of low concentrations. The most important features for this model occur at 819.79 nm (Na I lines at 819.704 nm and 819.708 nm), and 819.09 nm (Na I at 818.55 nm). (bottom) The LASSO model has several important coefficients, both positive and negative: 818.66 nm and 818.74 nm (Na I at 818.55 nm), 644.18 nm (Ca I at 644.09 nm), 445.61 nm (Ca I at 445.60 nm and 445.71 nm), and several coefficients, both positive and negative, related to the strong Na I doublet at 589.158 nm and 589.756 nm.

1151

1152 4.2.8. K₂O

1153 As shown in Figure 2, most samples in the LIBS data set have K₂O concentrations <6
 1154 wt.%. There are several samples between ~6 wt.% and ~10 wt.%, and two very high K₂O SCCTs:
 1155 TSRICH (37.99 wt.%; a mixture of BHVO-2 basalt and K-sulfate) and PMIOR (12.63 wt.%;
 1156 orthoclase). As a result of this distribution, it is challenging to train models that predict K₂O
 1157 accurately both in the 0 to 5 wt.% range and for higher potassium contents. The TSRICH
 1158 composition is so extreme that it is unrealistic to expect any model using our data set to predict it
 1159 reliably.

1160 Five models were considered in detail for the K₂O calibration, and they showed different
 1161 behaviors at low and high potassium concentrations. In general, the models presented a tradeoff
 1162 between the variability of predictions and performance at high K₂O contents. The PLS, ENet, and
 1163 LASSO models have broader variations for a given K₂O content, which results in negative
 1164 predictions for some low K₂O samples but perform better at high concentrations. The SVR and
 1165 Local ENet models are less noisy but tend to severely underestimate high K₂O compositions.

1166 We found that averaging the predictions of these five models resulted in slightly improved
 1167 performance for concentrations <10 wt.% compared to the LASSO model (low-concentration 3 m
 1168 RMSEP of 0.59 wt.% for averaging vs 0.64 wt.% for LASSO). Therefore the averaged result was

1169 selected as the initial preferred “model”. This averaging still resulted in negative values for some
1170 low-K₂O targets. In these cases, we set the potassium content to 0 wt.%.

1171 In our evaluation of the Mars results, we found the averaged results underpredicted both
1172 high K₂O SCCTs (PMIOR 12.63 wt.% and TSRICH 37.99 wt.%) while the LASSO model
1173 performed better on both targets. Although the LASSO predictions of TSRICH were still
1174 significantly low and highly variable, this is expected given the limitations of our data set. The
1175 Mars results were consistent with the laboratory results, but upon further discussion of the LASSO
1176 vs averaging results, we decided that the slight improvement of the averaged models over LASSO
1177 at low concentrations was not sufficient to sacrifice the better performance of LASSO at the high
1178 concentrations and we decided to switch to using the LASSO model alone as the preferred model.
1179 The 3 m test data set performance is shown in Figure 12. The RMSEP is 0.6, and the PMIOR
1180 target at 12.6 wt.% is predicted well. The test set predictions for targets with actual compositions
1181 between ~2-4 wt.% are grouped at ~3.5 wt.%. However, this behavior is not observed in the
1182 distribution of predictions from Mars (Figure 14). Mars SCCT results (Figure 13) include the
1183 extremely high K₂O TSRICH target, showing the predictions for this target vary widely from
1184 approximately correct to significant underprediction. Figure 23 shows the regression coefficients
1185 for the LASSO model, which relies heavily on the K II emission line at 438.94 nm, rather than the
1186 stronger K I lines at 766.7 nm and 770.1 nm.

1187 In the Mars results, the potassium content is mostly low, with steadily decreasing
1188 frequency toward higher concentrations (Figure 14). On the low end of this range, we observe
1189 that the model sometimes predicts negative values (which we set to 0 wt.% K₂O) for points that
1190 have potassium lines in their spectra, especially for points with high Mg, Ca or Fe content. This is
1191 not unique to LASSO; it is observed for all of the K₂O models considered. LIBS is highly sensitive
1192 to K₂O, particularly at the two strong K I emission lines mentioned above, so it is not surprising
1193 that at low K₂O contents, models with a RMSEP of ~1 wt.% may predict negative or zero K₂O
1194 contents when weak K₂O lines are still present. Blended submodels trained on an expanded
1195 training set could help to mitigate this behavior while also improving high K₂O predictions.

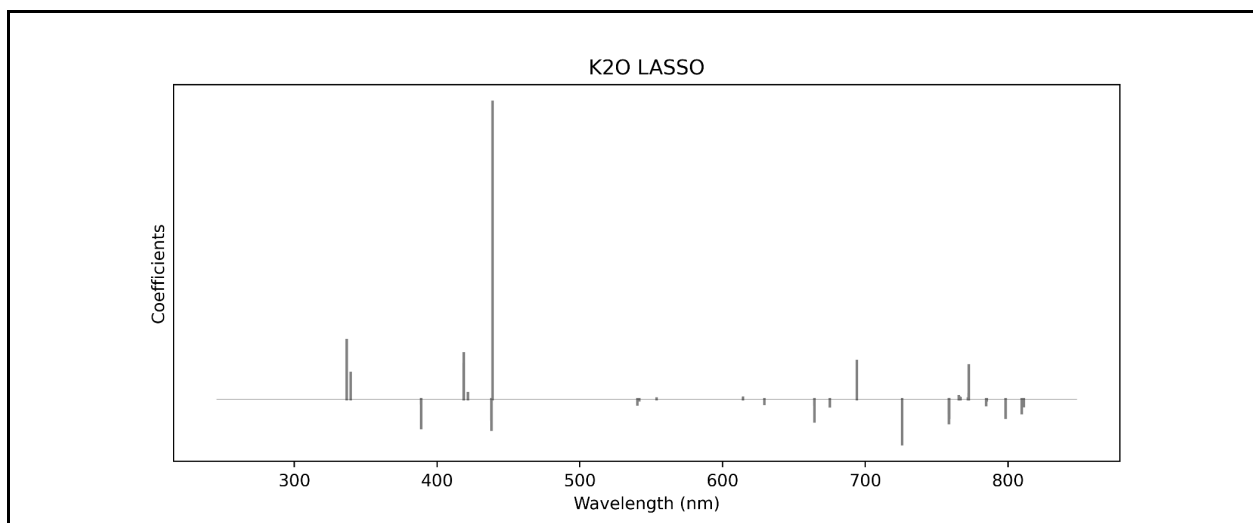


Figure 23: Regression coefficients for the K₂O LASSO model. The strongest coefficient is at

438.9 nm, which corresponds to K II at 438.94 nm.

1196 5. Discussion

1197 5.1. Accuracy

1198 The 3 m test set performance (RMSEP) provides an estimate of the accuracy of each
1199 regression model (Table 5), but in most cases the prediction accuracy varies with predicted
1200 composition and depends on the distribution of samples in the calibration data set. To provide
1201 the most representative estimate of the accuracy of each prediction, we calculate the RMSEP
1202 as a function of predicted concentration (“local RMSEP”) similar to that used for ChemCam [38].

Table 5: Summary of 3 m test set RMSEPs and selected models

Element	RMSEP wt. %	Model
SiO ₂	6.1	Average (GBR, PLS)
TiO ₂	0.3	RF
Al ₂ O ₃	1.8	Average
FeO _T	3.1	GBR
MgO	1.1	GBR
CaO	1.3	Blend RF+PLS
Na ₂ O	0.5	Blend GBR+LASSO
K ₂ O	0.6	LASSO

1203

1204 Local RMSEP is calculated for each element by first creating an evenly spaced array of
1205 simulated predicted values. For each simulated prediction, we calculate the RMSEP of the 60
1206 nearest test set predictions. As described in the Setup section, each target in the database was
1207 analyzed three times, so 60 test set predictions represent the nearest 20 targets. In cases
1208 where the distribution of test set compositions is sparse, a range of simulated predicted
1209 compositions may have the same nearest 60 test set predictions and therefore identical local
1210 RMSEPs. This is an artifact of the test set, and the “true” local RMSEP is assumed to vary
1211 smoothly. We handle these cases by removing duplicate values from the array of local
1212 RMSEPs. The local RMSEP values with duplicates removed are shown in black in Figure 24.
1213 After removal, we re-interpolate the RMSEP values, effectively creating a linear ramp in places
1214 where there was previously a “stair step.” To avoid neighboring predictions with significantly
1215 different RMSEPs, we smooth the RMSEP vs prediction curve such that it captures large-scale
1216 variations but removes small jumps in value.

1217 It is also necessary to extrapolate the local RMSEP values beyond the range of the test set.
1218 This is preferable to reporting no RMSEP at all for high predictions or reporting a “flat” RMSEP
1219 which would almost certainly underestimate the true uncertainty. We prefer to instead make an
1220 educated guess at the trend of RMSEP with predicted composition. With no test set data to

1221 compare with, extrapolated RMSEP values are speculative and should be used with caution.
1222 For most major elements, we calculate the slope of the extrapolated line based on a linear fit to
1223 the RMSEP values after removal of duplicates but prior to the re-interpolation. Since most
1224 elements have a general trend correlating RMSEP with predicted wt.%, this results in a line with
1225 a positive slope. Al_2O_3 is an exception: its RMSEP vs prediction curve rises and then drops back
1226 down, so a line fit to all of the RMSEP points has a nearly flat slope. We want our extrapolated
1227 local RMSEPs to be conservative, with the uncertainty increasing with the degree of
1228 extrapolation. So, for Al_2O_3 we instead fit the extrapolation line to only the RMSEP points from
1229 the minimum value at ~16 wt.% and above.

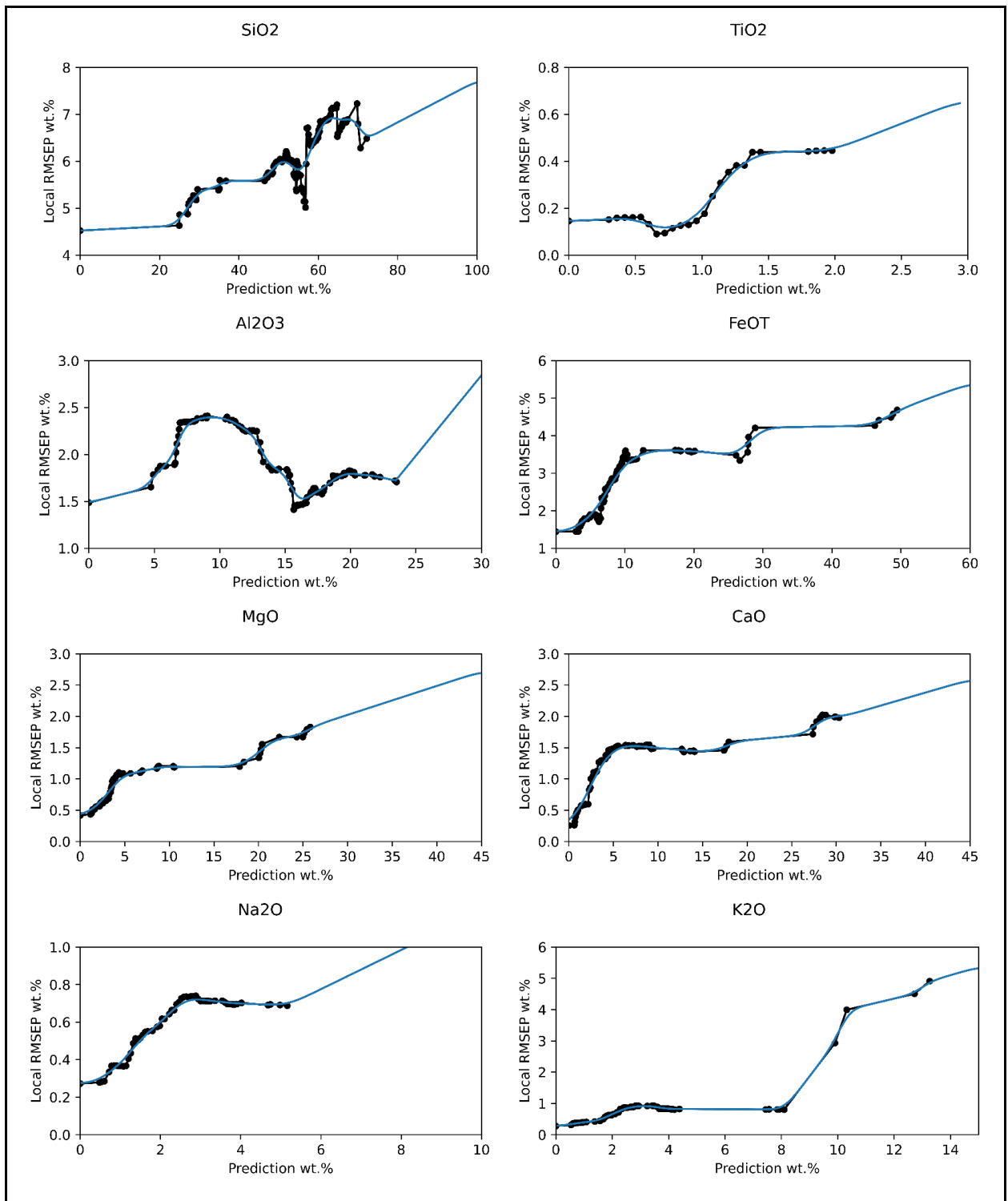


Figure 24: Local RMSEP vs prediction wt.% for each of the major elements. Black points are the unsmoothed values calculated using the nearest 60 test set predictions. Blue curves show the result of smoothing and extrapolating as described in the text.

1230 5.2. Precision

1231 According to the definition in ISO 5725-1:1994 [80], the accuracy of a model—how close its
1232 prediction is to the true value—is a combination of its trueness and precision. Trueness is how
1233 far the average prediction is from the true composition, while precision indicates the distribution
1234 of individual predictions around that average prediction value. RMSEP is a measure of the
1235 accuracy of our quantification, which is useful to understand when we compare derived
1236 abundances with stoichiometric mineral compositions or with abundances derived from other
1237 instruments (e.g., PIXL, ChemCam, APXS). Precision is important in determining whether
1238 groups of targets observed by the same instrument can be distinguished from one another [81].
1239 For example, to understand if the rover has entered a new geological formation by testing for a
1240 change in the distribution of chemical abundances [e.g., 15,81,82].

1241 We assess SuperCam precision in two ways. The first is to calculate the standard deviation of
1242 predictions across several locations on each target in the laboratory test set, assuming that
1243 these targets are homogeneous and that the predictions will be normally distributed. Then we
1244 take an average of the standard deviations across all targets. Effectively, this provides an
1245 estimate of the average spread around the typical predicted value expected in each oxide. Most
1246 standards were observed in three locations on the same target. Although standard deviations
1247 are usually computed from a larger number of samples, we apply it here on only three values for
1248 each standard. We argue that this statistic should be robust because we are averaging the
1249 standard deviations of ~60-70 standards, depending on the element. We find that the standard
1250 deviations are not correlated with concentration, so the mean standard deviation is taken in all
1251 cases (Table 6).

1252 A similar exercise can be conducted using the results from the SCCTs on Mars. This benefits
1253 from a greater number of observations per target, which makes the standard deviation estimate
1254 more robust. It also benefits from the fact that the measurements are made with the flight
1255 instrument on Mars rather than the laboratory instrument, making the precision estimates more
1256 relevant to measurements on Mars. In the Mars SCCT results, the standard deviations for high-
1257 MgO and high-Na₂O targets were somewhat higher than those for lower concentrations. In
1258 these cases we report the overall average precision and the precision with higher concentration
1259 targets excluded (the value in parentheses) in Table 6. The results for K₂O exclude the very
1260 high K₂O TSRICH target.

1261 Several factors affect the standard deviations from replicate measurements on standards. We
1262 suspect that some standards that are outliers in terms of standard deviations have larger grain
1263 sizes and/or more diverse compositions in individual grains despite efforts during sample
1264 preparation to homogenize the sample powders. Although the diameter of the laser beam is
1265 ~250 μm [2], the center of the beam can produce a large fraction of the ablation and emission,
1266 so grain sizes must ideally be much smaller than 50 μm. Other factors that will contribute to
1267 variations in reproducibility on surface targets include variations in focus, laser energy, and
1268 distance to the sample. On Mars, these factors will cause more day-to-day and sample-to-
1269 sample variations than are quantified in the test set standard deviations.

Table 6: Estimated precision for each of the major elements in wt.%. Numbers in parentheses exclude some higher concentration samples.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO _T	MgO	CaO	Na ₂ O	K ₂ O
3 m Test Set (Laboratory)	0.8	0.06	0.4	0.5	0.2	0.2	0.1	0.1
SCCTs (Mars)	1.6	0.02	0.7	1.3	0.5 (0.3)	0.5	0.3 (0.2)	0.3

1270 By comparing the values in Table 6 to the RMSEPs in Table 5 and Figure 12, we find that
 1271 SuperCam LIBS quantification is more precise than it is accurate, similar to the results from
 1272 ChemCam (e.g., [84]). Thus, although we strive to provide accurate stoichiometry, the greater
 1273 precision of the results combined with the ability to make frequent observations over the course
 1274 of the rover traverse, makes LIBS particularly useful for distinguishing trends in composition,
 1275 both within a single heterogeneous target, and across multiple targets.

1276 SuperCam’s estimated precision is comparable to that of ChemCam. Two measures of
 1277 ChemCam’s precision are given from repeated observations of its onboard calibration targets
 1278 [84] and of homogeneous, fine-grained bedrock [e.g.,81]. Many of the rocks encountered to date
 1279 in Jezero crater are heterogeneous at the scale of SuperCam LIBS points, so we do not yet
 1280 have enough observations of fine-grained rocks to provide an estimate of precision using data
 1281 from Mars surface targets.

1282 5.3. Environmental Factors

1283 As discussed above, numerous factors can cause changes in LIBS spectra, resulting in
 1284 changes in the quantitative results. These include shifts in wavelength calibration, variations
 1285 with distance and focus quality, and sensitivity to anomalous features in the spectra or faulty
 1286 continuum removal. Some factors can be assessed now, while assessing others would require
 1287 additional data collection either in the laboratory or on Mars.

1288
 1289 One effect that can be readily assessed with available data is the influence of shifts in
 1290 wavelength. Although we do not observe significant shifts in wavelength calibration in the Mars
 1291 data, slight shifts are unavoidable, and larger changes may occur due to changing seasonal
 1292 temperatures, observations conducted at unusual times of day, and changes in the instrument
 1293 itself over time. We trained our regression models on spectra that had been artificially shifted by
 1294 ±1 or 2 pixels to improve robustness to any shift that may occur. The peak binning
 1295 preprocessing used by some models also increases robustness to any shifts. Figure 25 shows
 1296 the 3 m test set RMSEP as a function of wavelength shift in pixels, with horizontal black bars
 1297 providing a reference value of 1.2 times the RMSEP without any shift. Within ±1 pixel of
 1298 wavelength shift, all models show little change in RMSEP.

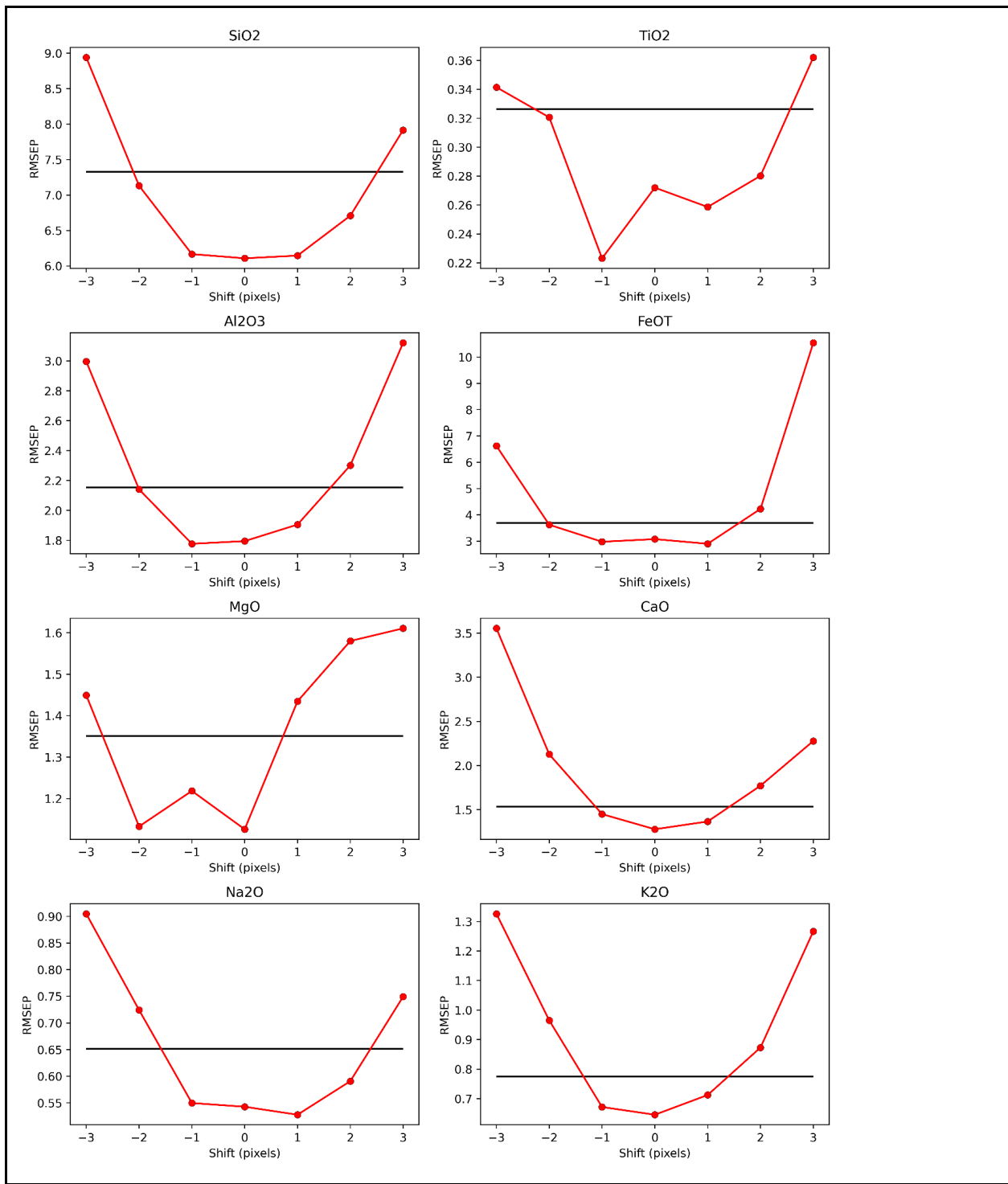


Figure 25: Test set RMSEP for each major element as a function of pixel shift. Horizontal black lines indicate a 20% increase in RMSEP relative to the value at 3 m. Wavelength shifts observed in Mars data correspond to less than 1 pixel of shift, which causes little variation in RMSEP for all elements.

1300 Distance effects have been observed in data from ChemCam. Multiple studies [85–87] observed
1301 that predicted abundances of several elements (Al, Na, K, and to some extent Si) increased as
1302 a function of distance. For SuperCam, our models have the advantage of being based primarily
1303 on data acquired at 3 m, whereas the ChemCam models were trained on data acquired at 1.5 m
1304 [38]. The SuperCam models were also selected based in part on robustness to distance trends.
1305 However, additional Mars data at varying distances may still reveal a distance effect, particularly
1306 since SuperCam has shown greater ability than ChemCam to observe targets at long distances.
1307 SuperCam LIBS operates at least to 8.75 m compared to ChemCam’s longest observation of
1308 ~7.2 m on bedrock. Both instruments are able to achieve a LIBS spark at even longer
1309 distances on iron meteorites (due to iron’s excellent absorption of the laser), which are
1310 encountered occasionally on the surface of Mars. However, pure metal targets have significantly
1311 different matrix effects than typical geologic targets composed of oxides and must be handled
1312 separately. As additional data are collected on Mars, especially on fine-grained, uniform
1313 geologic units, it will be possible to better assess distance effects and develop methods to
1314 mitigate it.

1315 We do not have laboratory data suitable to assess variations in results due to changing focus. Such
1316 data could be collected on Mars, either as a dedicated experiment or over the course of the
1317 mission, as occasional observations with poor focus are inadvertently acquired. The effects of
1318 poor focus are similar to the effects of distance in that the laser energy per unit area on the target
1319 is decreased. Thus, it may be that a distance correction (if needed) also can help to mitigate the
1320 effects of poor focus.

1321 In Mars data, we have observed a bump in the baseline of processed data that covers several
1322 nm around 290 nm in the UV spectrometer that was not present in the cleanroom data. The origin
1323 of this feature is not well understood and still under investigation, but it may be related to the SiO₂
1324 content of the target. We are currently testing a correction to the continuum removal algorithm
1325 parameters for the UV spectrometer to remove the bump. Alternatively, or in addition, it may be
1326 possible to remove the anomalous bump using calibration transfer methods, as described below.

1327 5.4. Future Work

1328 Although the current models selected for the major elements are acceptable, they could be
1329 improved. In addition, developing methods by which new spectra could be evaluated prior to
1330 quantification would ensure that they are similar enough to the training data set to give accurate
1331 results. The sections discussing Spectral Variability and Outlier Removal above suggest
1332 possible approaches to evaluating and identifying outliers that could be applied to the Mars
1333 data. In addition, it may be beneficial to develop tests to verify the presence of emission lines
1334 from an element prior to predicting it.

1335 5.4.1. Uncertainty Quantification

1336 Although our calculation of Local RMSEP seeks to provide an estimate of the uncertainty of a
1337 prediction as a function of composition, it is not able to account for the possibility that the “true”
1338 uncertainty in the predicted composition may be different even for the same predicted composition.

1339 For example, two samples may have the same SiO₂ content, but one may have significantly
1340 more FeO_T and as a result have an increased uncertainty in the predictability of SiO₂. Under our
1341 current scheme, the local RMSEP at a certain predicted SiO₂ content is constant, regardless of
1342 any other factors. Additionally, while the extrapolated Local RMSEP values are a better solution
1343 for predictions outside the training set than simply providing a constant RMSEP, it should be
1344 possible to achieve a more statistically rigorous estimate of uncertainties in these cases. One
1345 approach is to use Bayesian regression methods, which are inherently based on probability
1346 distributions. Rather than returning a single value, they return a distribution of predictions for
1347 each unknown spectrum. Statistical measures, such as the mean and standard deviation of that
1348 distribution, can be used to describe the model's "best" prediction and its associated
1349 uncertainty. Preliminary work on quantifying LIBS using gaussian process variational
1350 autoencoders [88] is promising, and has additional benefits such as the ability to estimate the
1351 spectrum corresponding to a given composition, with uncertainties on the estimated spectrum.

1352 5.4.2. Minor and trace elements

1353 Minor and trace elements are important to quantify because they provide distinctive tracers
1354 among largely similar rock targets, related to their primary petrogenesis (i.e. magmatism) and
1355 information about past alteration. Such elements typically present only a few detectable
1356 emission lines, which are relatively weak compared to the lines from major elements. Both
1357 univariate and multivariate methods have been used to quantify minor and trace elements with
1358 LIBS.

1359
1360 For the ChemCam instrument, several methods were investigated for quantifying trace
1361 elements. Ollila et al. [89] developed univariate and multivariate (PLS) models for the
1362 quantification of Li, Rb, Sr, and Ba. For Li, they found that the univariate model was more
1363 accurate than the PLS models. However, for Rb, Sr, and Ba, the univariate and PLS models
1364 gave similar results. [36] revised the quantification of these elements, using univariate models
1365 and the updated ChemCam database with more than 400 samples [38]. The updated
1366 quantification showed improvement for Li and Ba and similar results for Rb and Sr, although a
1367 direct comparison of RMSE is difficult because the range of compositions in the models was
1368 different.

1369
1370 Mn is an important element to quantify because it provides information about redox and pH of
1371 the ancient martian environment. It was first quantified for ChemCam using a univariate
1372 approach [31] based on a database of ~60 samples. Then, using the expanded database from
1373 [38] with additional Mn-bearing samples, [90] developed an improved quantification for Mn,
1374 based on blended multivariate submodels.

1375
1376 Several other minor/trace elements are quantified with ChemCam: Cl, H, S, P, Ni, F, Zn [e.g.
1377 48,51,90–92]. Quantification of minor and trace elements to which LIBS is relatively sensitive
1378 (Li, Rb, Sr, Ba, and Mn) is likely to be more straightforward, while elements with weaker spectral
1379 lines (Cl, S, H, P, Ni, F) will likely be more challenging.

1380

5.4.3. Alternative Normalization

1381 Prior to significant efforts to revise the major element calibration or develop new calibrations for
1382 trace and minor elements, it would be prudent to review the preprocessing steps applied to the
1383 spectra before quantification, such as normalization. Although normalization helps to correct for
1384 fluctuations intrinsic to the LIBS process, and to mitigate distance, focus, and signal quality
1385 effects, the normalization scheme itself can introduce artifacts. Our normalization is currently
1386 applied after the continuum has been removed. Because of this, the sum of the signal in each
1387 spectrometer by which the spectrum is divided, is highly dependent upon the composition of the
1388 target [25]. For example, consider two targets with identical Ca content, one with a very high Fe
1389 content and one with very low Fe. Fe has numerous emission lines, particularly in the UV
1390 spectrometer. Thus, the high-Fe sample will be divided by a larger number (the sum of the
1391 emission lines) effectively resulting in “smaller” Ca lines compared to the other target, despite
1392 having identical Ca content.

1393 Finding an alternative method of normalization that can avoid these issues may be possible One
1394 possibility is to divide the spectrum in each spectrometer by the total of the continuum in that
1395 spectrometer, which is far less influenced by the composition of the target than the total of the
1396 emission lines. However, part of the initial motivation for removing the continuum before
1397 normalization was to mitigate distance effects. Normalizing by the continuum may reduce
1398 normalization artifacts related to composition at the expense of stronger artifacts due to
1399 distance, necessitating a separate distance correction.

1400

5.4.4. Calibration Transfer

1401 Although the application of the instrument response function corrects for the most significant
1402 differences between spectra collected in the laboratory and those collected on Mars, there are
1403 still differences. The origin of these differences is not fully understood, but they represent a
1404 common scenario in chemometrics, where a calibration was developed using data from a
1405 specific instrument in certain conditions and then is implemented on another instrument or the
1406 same instrument in different conditions. The process of correcting for such differences is
1407 referred to as “calibration transfer,” and various methods are available for performing this task.
1408 In general, calibration transfer relies on a set of spectra collected by both instruments to derive
1409 a transformation that can be applied to one or both sets of spectra to minimize differences and
1410 enable accurate intercomparison. For ChemCam, a simple calibration transfer approach based
1411 on the average ratio between rover calibration target spectra from Mars and those in the
1412 laboratory was used by Clegg et al. [38]. Similarly, for SuperCam the SCCTs provide the suite
1413 of common spectra on Earth and Mars.

1414

1415 We have begun investigating calibration transfer corrections that may improve the performance
1416 of our quantifications. In Figure 26, we show the results of applying the piecewise direct
1417 standardization (PDS) calibration transfer method [94] to the lab SCCT data. We find the
1418 transformed data are spectrally ‘closer’ to the Mars data by examining the distance between the
1419 principal components of Mars and laboratory spectra before and after calibration transfer.

1420 Additional work is needed to assess the influence of calibration transfer on quantification and to
1421 understand how the differences in laser power between SCCT and Mars surface target
1422 observations affect the correction.

1423
1424
1425

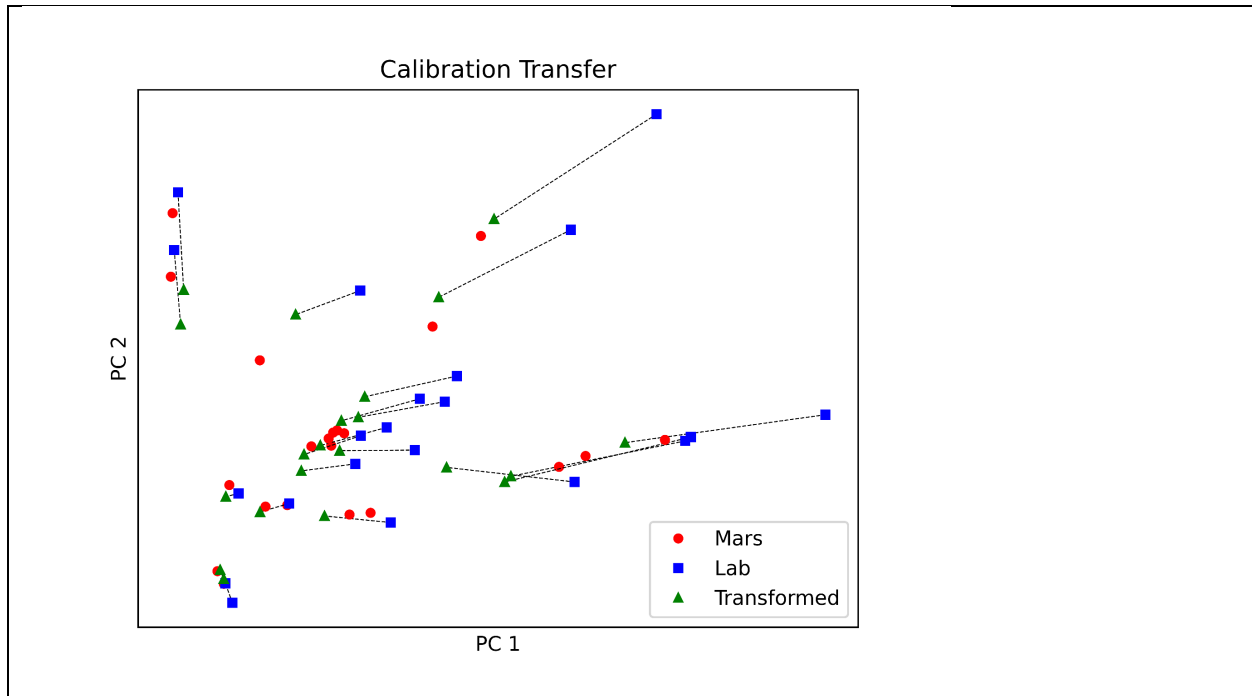


Figure 26: PCA scores plot comparing average Mars spectra for each SCCT (red circles) with the corresponding average spectra from the laboratory (blue squares). Laboratory spectra with Piecewise Direct Standardization (PDS) calibration transfer applied are shown as green triangles. Dashed lines connect the untransformed and transformed lab data points. In general, calibration transfer brings the laboratory spectra closer to the corresponding Mars spectra.

1426
1427

1428 6. Conclusion

1429 This paper represents a summary of the current status of SuperCam LIBS quantification efforts.
1430 By using a suite of 1198 laboratory spectra of 334 diverse standards, we have developed
1431 multivariate regression models for the quantification of the major elements SiO_2 , TiO_2 , Al_2O_3 ,
1432 FeO_T , MgO , CaO , Na_2O , and K_2O . Initial model selection was based primarily on test set
1433 RMSEPs and early results from Mars. With additional data from Mars, we were able to identify
1434 issues with the initial calibration which were not apparent in laboratory data alone and adjust the
1435 selected models accordingly to eliminate or reduce the issues identified. Although many areas
1436 of potential improvement remain, the SuperCam major element calibration is more mature than
1437 the ChemCam calibration was at a similar point in the mission. As additional data are collected

1438 on Mars and in the laboratory, it will be possible to continue to improve SuperCam's quantitative
1439 LIBS capabilities, which play a fundamental role in the *Perseverance* rover's science mission.

1440

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