

**Key Points:**

- Principal component and spectral parameter analysis of Chemistry and Camera (ChemCam) passive spectra highlight four spectral end-members in Mt. Sharp group rocks
- A decrease in the near-infrared slope is seen in the Hutton interval, suggesting a changing depositional environment or enhanced diagenesis
- Bedrock containing Mg-sulfates and Ca-sulfate cements are highlighted in a multivariate survey of ChemCam passive spectra

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Compositional Variations in Sedimentary Deposits in Gale Crater as Observed by ChemCam Passive and Active Spectra

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Abstract During the first 2934 sols of the Curiosity rover's mission 33,468 passive visible/near-infrared (NIR) reflectance spectra were taken of the surface by the mast-mounted Chemistry and Camera (ChemCam) instrument on a range of target types. ChemCam spectra of bedrock targets from the Murray and Carolyn Shoemaker formations on Mt. Sharp were investigated using principal component analysis and various spectral parameters including the band depth at 535 nm and the slope between 840 and 750 nm. Four end-member spectra were identified. Passive spectra were compared to Laser Induced Breakdown Spectroscopy (LIBS) data to search for correlations between spectral properties and elemental abundances. The correlation coefficient between FeO_T reported by LIBS and BD535 from passive spectra was used to search for regions where iron may have been added to the bedrock through oxidation of ferrous-bearing fluids but no correlations were found. Rocks in the Blunts Point-Sutton Island transition that have unique spectral properties compared to surrounding rocks, that is flat NIR slopes and weak 535 nm absorptions, are associated with higher Mn and Mg in the LIBS spectra of bedrock. Additionally, calcium-sulfate cements, previously identified by Ca and S enrichments in the LIBS spectra of bedrock, were also shown to be associated with spectral trends seen in Blunts Point. A shift toward a steeper NIR slope is seen in the Hutton interval, indicative of changing depositional conditions or increased diagenesis.

Plain Language Summary The Chemistry and Camera (ChemCam) instrument on the Mars Science Laboratory Curiosity rover was built for use in “active” mode, in which a laser vaporizes a small amount of material from a targets' surface and the light emitted from the resulting plasma is used to quantify the relative amounts of various elements. ChemCam also collects “passive” spectra (without the use of the laser). These passive spectra use reflected sunlight to provide complementary mineralogical information. By looking at how passive and active spectral features relate and change, we can further our understanding of the composition of targets that the rover has encountered. Specifically, this methodology can help determine if Curiosity encountered rocks altered by fluids containing reduced iron. Comparison between passive spectral parameters and iron oxides reported by active spectroscopy identified two regions (Sutton Island to Blunts Point and Glasgow to Knockfarril Hill transitions) as areas of compositional interest and show evidence of variations in oxidation conditions. The passive spectra are also shown to be largely in agreement with data from Chemistry and Mineralogy, another instrument on Curiosity which provides mineralogical analysis of powdered samples.

1. Introduction

The Mars Science Laboratory's (MSL) Curiosity rover landed on the northern plains of Gale Crater, a ~154 km diameter impact crater in southern Elysium Planitia, along the planetary dichotomy in August of 2012. Since landing, Curiosity has traveled across the crater floor and then up the side of Mt. Sharp (formally known as Aeolis Mons) with a goal to characterize the past environments preserved in the region's sedimentary rock record and to determine if these environments would have been habitable (Vasavada, 2022 and references therein).

Visible and near-infrared (VNIR; ~400–1,000 nm) reflectance spectroscopy plays a key role in the suite of tools Curiosity uses to identify the composition of materials it encounters. This spectral range is sensitive to broad charge-transfer and crystal field absorptions that are most commonly associated with iron-bearing minerals (e.g.,

Wellington et al., 2017). Curiosity's Mast Camera (Mastcam) measures the relative reflectance of the surface from 400 to 1,020 nm in up to 12 unique wavelengths (Bell et al., 2017; Malin et al., 2017). Multispectral observations have been demonstrated to discriminate compositionally distinct materials in the Gale Crater, and they qualitatively agree with mineralogy from samples measured by Curiosity's X-ray diffraction instrument (Horgan et al., 2020; Jacob et al., 2020; Wellington et al., 2017). Large-scale surveys of the VNIR spectral properties of rocks, soils, and veins along Curiosity's traverse conducted using Mastcam data from sols 0–2302 have been interpreted to reveal nine rock spectral classes (Rice et al., 2022). The spectral differences between classes were understood to be caused predominantly by variations in grain size and abundance of hematite and other iron oxides (Rice et al., 2022). Rock spectral variability was also observed to align with stratigraphic members in some cases (Horgan et al., 2020; Rice et al., 2022).

Early in Curiosity's mission, a novel protocol was developed to calibrate passive radiance measurements from the Chemistry and Camera (ChemCam) (i.e., without the use of ChemCam's laser) to relative reflectance using well-characterized Mastcam and ChemCam calibration targets, creating a VNIR relative reflectance spectra data set (Johnson, 2022; Johnson et al., 2015). In contrast to Mastcam, which is an imager, ChemCam collects point spectra from spots that are nanometers to micrometers in size. Like Mastcam spectra, ChemCam relative reflectance spectra proved useful in classifying material near Curiosity's landing site and observing airfall dust coverage and have been shown to be sensitive to mineralogy, with the ability to distinguish major Fe-bearing minerals (e.g., hematite and ferric sulfates) in Mt. Sharp, sometimes as far away as several kilometers (Johnson et al., 2015, 2016). ChemCam passive spectra have also been demonstrated to be consistent with Chemistry and Mineralogy (CheMin) X-ray diffraction data (Johnson et al., 2016; Wellington et al., 2017).

In active mode, ChemCam uses laser ablation in the form of Laser Induced Breakdown Spectroscopy (LIBS) to investigate rocks and regolith in Gale Crater (Maurice et al., 2012; Wiens et al., 2012). LIBS provides information about the elemental composition of geologic materials and is especially valuable because it can be used to investigate targets several meters away, removes most of the airfall dust from the observation area (Graff et al., 2011; Johnson et al., 2015), and has the ability to sense chemical changes with depth (Lanza et al., 2012). ChemCam acquires a passive spectrum before and/or after each LIBS observation, so almost all the passive reflectance spectra pair one-to-one with a LIBS elemental abundance measurement. The correlated LIBS elemental chemistry and passive spectral data sets therefore provide a unique resource to track how the reflectance properties and chemical composition varied over the course of the traverse at the nanometer to micrometer scale.

This paper expands upon and complements previous investigations of ChemCam passive and Mastcam spectral data of rocks in the lower portion of Mt. Sharp (Fraeman et al., 2020; Haber et al., 2022; Horgan et al., 2020; Jacob et al., 2020; Johnson et al., 2015, 2016; Rice et al., 2022; Wellington et al., 2017). Here, the spectral properties of bedrock targets in Mt. Sharp's Murray and Carolyn Shoemaker formations observed by ChemCam passive spectra are studied using principal component analysis (PCA) along with band depth and spectral slope/ratio calculations. This spectral data set comprises a subset of 9,400 passive spectra acquired between sols 776 and 2934 of Curiosity's mission. This work also for the first time investigates paired ChemCam LIBS elemental composition data and passive reflectance spectra with the goal to investigate the source(s) and implications of spectral trends seen in the ChemCam passive data set. Where available, ChemCam data are also compared with the mineralogy reported by the CheMin instrument to search for further insight into sources of spectral variability.

2. Background

2.1. Mount Sharp Geology

Gale Crater is a ~3.7-billion-year-old impact feature near the boundary of the northern highlands and southern lowlands of Mars (e.g., Pelkey & Jakosky, 2002). Gale Crater contains a central mound, Mount Sharp, that rises ~5.5 km above the surrounding terrain (e.g., Thomson et al., 2011) and provides an unprecedented opportunity to examine hundreds of meters of stratigraphy that may preserve clues to the past climate history and habitability of Mars.

The sedimentary rocks that Curiosity has traversed can be divided into three geologic groups: (a) the Bradbury group, where Curiosity landed and explored the first 776 sols of its mission, is composed of diverse sedimentary units including fluvial, aeolian, and lacustrine deposits along the crater floor; (b) the Mount Sharp group, which is the sedimentary group that makes up the primary structure of Mount Sharp; and (c) the Siccar Point group,

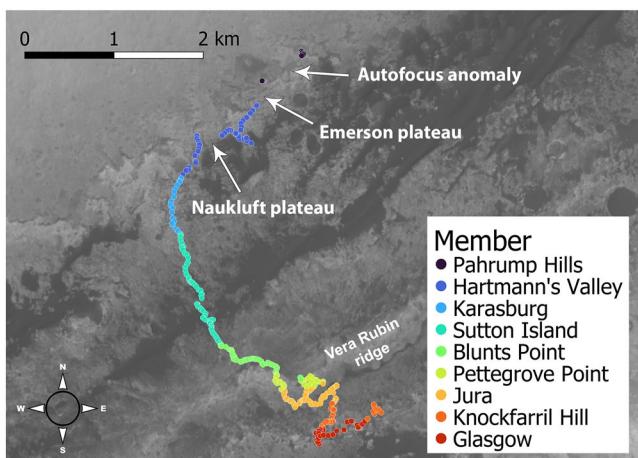


Figure 1. All ChemCam bedrock targets in the Murray and Carolyn Shoemaker formations, up to sol 2934, colored by stratigraphic member (Table 1). Gaps in the earlier part of the data are due to traversing aeolian strata at Emerson and Naukluft Plateaus, and to a temporary anomaly with ChemCam's autofocus. Knockfarril Hill and Glasgow are part of the Carolyn Shoemaker formation, all other members are part of the Murray Formation. The base map is a CTX 6 m mosaic (Calef & Parker, 2016).

Sherman, 1985; D. M. Sherman & Waite, 1985; V. M. Sherman et al., 1982). Poorly crystalline, nanophase Fe oxides lack these distinct spectral absorptions and are characterized by a steep spectral edge between 400 and 750 nm (Bell et al., 1990, 2000). Magnetite, a mixed-valence Fe oxide, has a relatively flat, low-reflectance spectrum with a local minimum near 550 nm and local maximum near 650 nm, caused by closely colocated Fe^{2+} and Fe^{3+} in both tetrahedral and octahedral coordination (Izawa et al., 2019). Although a variety of factors (e.g., particle size, opaque minerals) can influence the strength of an absorption band in reflectance spectra, calculating relevant band depth, band positions, and spectral slopes can provide a measurement of relative absorption strength between samples.

3. Methods

3.1. ChemCam Passive Spectral Data Acquisition and Treatment

ChemCam passive surface spectral data calibrated to relative reflectance using the methods described in Johnson et al. (2015, 2016) are available from NASA's Planetary Data System (PDS) Geosciences Node (Johnson, 2022).

Table 1
Stratigraphic Members in the Mt. Sharp Group

Stratigraphic formation	Stratigraphic member	Approximate sol range	Elevation relative to MOLA datum (m)
Murray	Pahrump Hills	776–797, 807–950, 997–1035, 1067–1072	-4,460 to -4,437
Murray	Hartmann's Valley	1105–1108, 1154–1276, 1354–1412	-4,437 to -4,412
Murray	Karasburg	1413–1473	-4,412 to -4,375
Murray	Sutton Island	1474–1690	-4,375 to -4,280
Murray	Blunts Point	1691–1809, 2046–2094	-4,280 to -4,210
Murray	Pettegrove Point	1810–1873, 2000–2014, 2024–2045, 2095–2157	-4,210 to -4,172
Murray	Jura	1874–1999, 2015–2023, 2158–2439, 2448–2453	-4,172 to -4,143
Carolyn Shoemaker	Knockfarril Hill	2440–2447, 2454–2606, 2817–2950	-4,143 to -4,117
Carolyn Shoemaker	Glasgow	2607–2695, 2735–2816	-4,117 to 4,072

Note. Geological member/formation sol (Martian day) ranges and elevations (Edgar et al., 2020; Fedo et al., 2022; Gwizd et al., 2022; Stack et al., 2016).

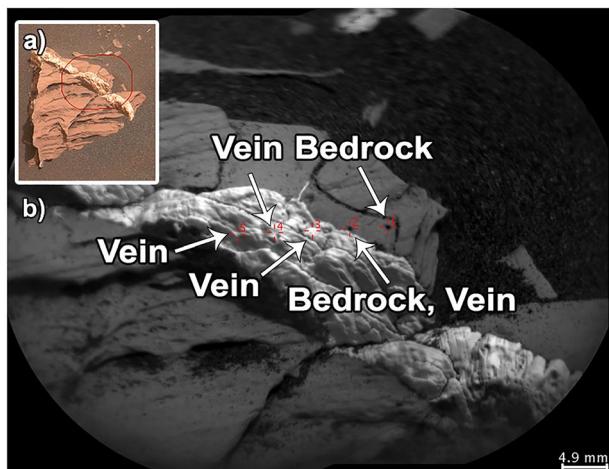


Figure 2. Example of different types of ChemCam target materials (target Tofte on sol 2080). (a) The red ellipse in this Mastcam mosaic context image shows the location of the ChemCam Remote Micro Imager (RMI). (b) Each of the red crosshairs in this RMI image corresponds to a Laser Induced Breakdown Spectroscopy and passive spectral target. Target type classifications for each point are shown.

veins, calibration targets, soils, and sands. An example of 1×5 ChemCam raster target that covers vein, bedrock, and mixed vein and bedrock-classified material is shown in Figure 2. Of the 33,631 passive spectra taken in the first 2934 sols, 16,246 (48.3%) are solely categorized as bedrock targets. Only Murray and Carolyn Shoemaker formation targets classified as “bedrock” collected prior to sol 2934 were included in the analyses described below (9,400 observations). It is important to note that LIBS measurements give information about a smaller radius of material due to the narrower size of the laser beam compared to the spectrometer IFOV ($\sim 400 \mu\text{m}$ for the laser spot size vs. $\sim 1.3\text{--}2.6 \text{ mm}$ for the ChemCam passive spectral for targets 2–4 m away; Maurice et al., 2012; Wiens et al., 2012), so their sampling areas are different. Only bivariate correlations between LIBS and passive spectral parameters were considered for simplicity and interpretability. Given the complicating role of the field of view, hierarchical multivariate methods (e.g., Karunatillake et al., 2012) could prove useful in future studies.

3.2. Spectral Characterization

The shape and location of spectral absorption, as well as the overall shape of the spectrum itself, can be described by numerical parameterizations such as band depths and spectral slopes. Previous studies have found several spectral parameters that are particularly effective for evaluating characteristics of ChemCam passive spectra, summarized in Table 2 (Johnson et al., 2015, 2016). Band shapes and positions have been determined to be resilient to ChemCam calibration uncertainties (Johnson et al., 2016).

Two prominent spectral parameters used here were the band depth at 535 nm (BD535) and slope between 840 and 750 nm (S7584) (Table 2). The absorption at 535 nm is caused by the presence of ferric phases. The slope from 840 to 750 nm can be a proxy for a broad absorption feature centered at ~860 nm, which is related to some ferric phases such as hematite (Morris et al., 1985), although it can also be sensitive to the broad Fe²⁺ absorption near 1,000 nm associated with olivine and pyroxene. Combined, large BD535 and S7584 values have been confirmed to provide evidence for the presence of ferric phases (Fraeman et al., 2020; Jacob et al., 2020; Wellington et al., 2017).

3.3. LIBS Elemental Abundance Data

ChemCam LIBS spectra were converted into major oxide compositions (MOCs) via a calibration model that uses a weighted average of two multivariate approaches: partial least squares and independent component analysis (Clegg et al., 2017). This model was trained on a diverse set of 408 pressed power samples with independently measured

ChemCam uses three spectrometers to measure reflected radiance: the UV spectrometer (240.1–342.2 nm), violet (VIO) spectrometer (382.1–469.4 nm), and VNIR spectrometer (474.0–906.5 nm) (Wiens et al., 2012). Estimated 3-sigma absolute calibration uncertainties on landing for the three spectrometers were ~6% (VNIR), ~8% (VIO), and ~20% (UV) (Johnson et al., 2015). Passive spectra are restricted to 440–840 nm because the UV spectrometer responsivity, VIO spectrometer responsivity <440 nm, and VNIR spectrometer responsivity >840 nm are relatively low, resulting in low signal-to-noise ratio (SNR) in the passive reflectance spectra (Johnson et al., 2015). Data near the detector edges around the gap between the VIO and VNIR spectrometers, from ~469 to 474 nm, are also associated with low SNR due to low detector responsivity (Wiens et al., 2012). The trimmed spectra were passed through a Savitzky-Golay filter (SG) for smoothing, which fit subsets of nearby points with a cubic polynomial via linear least squares (Savitzky & Golay, 1964). This smoothing step ensured that the spectral features were not a result of localized noise. Spectra that had at least one negative value for relative reflectance between 440 and 840 nm after filtering (256 spectra) were deemed invalid and removed from the data set. Spectra were coregistered with orbital basemaps using QGIS, and MSL localizations from the sol the spectra were acquired were used to assign each measurement a latitude and longitude (Deen, 2015).

ChemCam surface reflectance passive spectra of each observation were manually classified by Johnson (2022) into target types such as bedrock, sand. An example of 1×5 ChemCam raster target that covers vein, bedrock, sified material is shown in Figure 2. Of the 33,631 passive spectra taken in the e solely categorized as bedrock targets. Only Murray and Carolyn Shoemaker rock” collected prior to sol 2934 were included in the analyses described below nt to note that LIBS measurements give information about a smaller radius of of the laser beam compared to the spectrometer IFOV ($\sim 400 \mu\text{m}$ for the laser ChemCam passive spectral for targets 2–4 m away; Maurice et al., 2012; Wiens as are different. Only bivariate correlations between LIBS and passive spectral mplexity and interpretability. Given the complicating role of the field of view, (e.g., Karunatillake et al., 2012) could prove useful in future studies.

Table 2*Equations to Calculate Spectral Parameters (Fraeman et al., 2020; Johnson et al., 2015)*

Spectral parameter	Equations	Description
BD535	$1 - \frac{R_{535}^*}{0.65R_{500}^* + 0.35R_{600}^*}$	Positive when Fe ³⁺ is present
BD600	$1 - \frac{R_{600}^*}{0.52R_{535}^* + 0.48R_{670}^*}$	Related to the strength of the short wavelength ferric oxide absorption edge
R6744	$\frac{R_{670}^*}{R_{440}^*}$	VIS ratio, related to airfall dust coverage
R6084	$\frac{R_{840}^*}{R_{600}^*}$	NIR ratio
S7584	$\frac{R_{840}^* - R_{750}^*}{(840-750)}$	NIR slope, indicative of the strength of iron absorptions
Spectral maximum	NA	Wavelength at which R^* is highest.
Average relative reflectance	$\frac{\sum R^*}{2462}$	Average relative reflectance of a target from 440 to 840 nm

Note. $R^*_{\#\#\#}$ is the relative reflectance after smoothing with the Savitsky-Golay filter at $\#\#\#$ nm. Average relative reflectance is the sum of the relative reflectance divided by the total number of channels between 440 and 840 nm (2462).

compositions and cross validation was used to tune relevant modeling parameters. The result is MOC tables that report the wt% of various oxides as well as the corresponding Root Mean Squared Error of Prediction values for all points analyzed by LIBS. These MOC tables are available from the PDS Geosciences Node (Wiens, 2022).

ChemCam acquires a passive spectrum before or after each LIBS observation, so almost all the passive spectra of bedrock in the Murray and Carolyn Shoemaker formations pair one-to-one with a LIBS elemental abundance measurement. The correlated LIBS elemental chemistry and passive spectral data set allow for tracking how the spectral properties compare with chemical composition, and how both changed over the course of the traverse. Although data were acquired between sols 801 and 985, during the resolution of the ChemCam autofocus problem (Peret et al., 2016), the mode of observation during this period makes it more difficult to match LIBS and passive spectra, so this period was not considered in this study (Figure 1). There is also a subset of “passive only” targets, where data were collected without LIBS (Johnson et al., 2015, 2016), and those targets are also not included in this work. All major oxides reported by ChemCam (FeO_T , MgO , SiO_2 , CaO , Na_2O , K_2O , TiO_2 , and Al_2O_3) were included in the analysis, as was MnO (Gasda et al., 2021). Iron abundances are given as FeO, regardless of the actual oxidation state, because the oxidation state is not determined by routine LIBS analysis.

3.4. Principal Component Analysis

PCA is a dimensionality reduction technique which converts an n-dimensional data cloud into orthogonal principal components (PCs) sorted from high to low percentages of the variance in the data set that can be summarized with only a few axes to aid in analysis (Pearson, 1901). PCA was conducted on the passive spectral data from ChemCam using the scikit-learn library in Python (Pedregosa et al., 2012). To understand the influence of compositional features on the data set and subsequent major PCs, the PCs were plotted against each other, spectral parameters (as described in Section 3.2), and LIBS elemental abundances. Correlations were reported using Spearman’s rank correlation coefficient, which describes how well the relationship between two variables can be expressed as a monotonic function (Spearman, 1904). PCA has proved useful in capturing the variability of ChemCam LIBS spectra (R. B. Anderson et al., 2011) and has also been applied to analyses of planetary reflectance spectral data sets (Farrand et al., 2013). Loading plots show the wavelength contributions to each PC and were very helpful in interpreting the meaning of PC values. Positive loadings for a PC in a given wavelength region mean that higher reflectance in that range would lead to higher values for that PC; negative loadings for a PC in a given wavelength region mean that higher reflectance in that range would lead to lower values for that PC. The terms “contribute positively” and “contribute negatively” (to a given PC) are used to describe positive and negative loadings. The distance from zero indicates the relative influence at a given wavelength.

3.5. CheMin Data

The CheMin instrument uses X-ray diffraction to measure the presence and abundance of minerals and X-ray amorphous materials in drilled rock and scooped soil samples in Gale Crater (Blake et al., 2012). CheMin

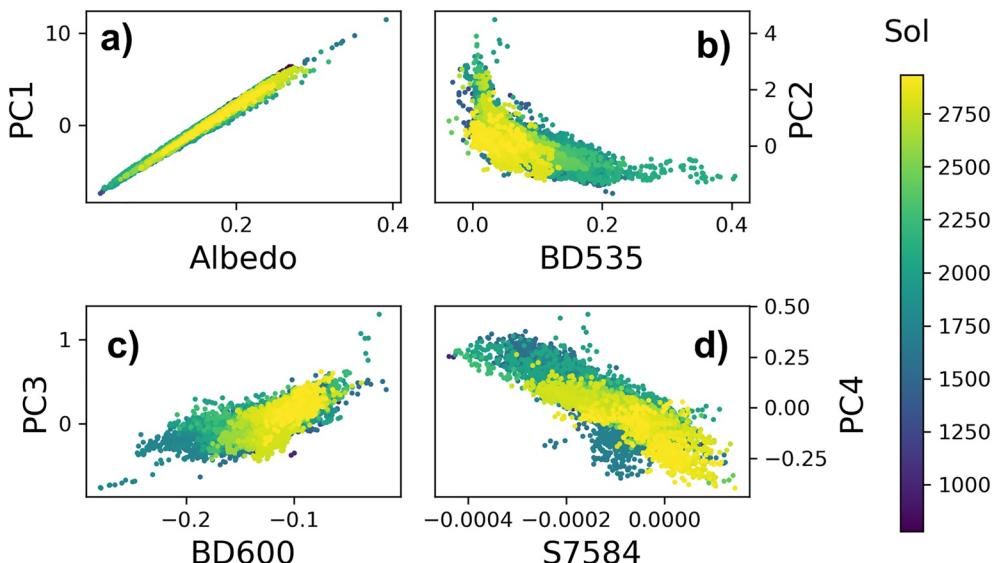


Figure 3. (a) PC1, (b) PC2, (c) PC3, and (d) PC4 plotted against spectral parameters. Negative band depth values indicate that the spectrum is concave at that wavelength. Colored by sol.

observations were compared to ChemCam passive spectral parameters to see how ferric minerals affect the relative reflectance data. CheMin requires sample processing (i.e., drilling or scooping), and as a result there are far fewer observations compared to ChemCam. CheMin typically analyzes a sample drilled from a depth of 3–4 cm (R. C. Anderson et al., 2012), whereas ChemCam only probes a few micrometers below the surface per laser shot (Maurice et al., 2012). Analyses of CheMin data identify ~20%–70% X-ray amorphous materials in every sample measured to date, and it is very difficult to characterize the identity of the amorphous material(s) from the XRD data alone (Rampe, Blake, et al., 2020). The amorphous component may have a substantial impact on the target's reflectance data because mass balance calculations of the amorphous component composition using CheMin and APXS data suggest that the amorphous component is typically enriched in FeO_T, potentially corresponding to nanophasic ferric oxides (e.g., Rampe, Blake, et al., 2020).

4. Results

4.1. Principal Component Analysis

The first PC1 accounted for 92.62% of the variance in the data set and was strongly correlated with average relative reflectance (Spearman's $\rho = 0.99$; Figure 3a). PC1's loadings were all positive and mirrored the average ChemCam reflectance spectrum, as expected (Figure 4a). PC2 explained 6.61% of the variance and was negatively correlated with BD535 (Figure 3b) and R6744 and positively correlated with R6084 ($\rho = -0.73$, -0.90 , and 0.80 , respectively). The wavelength range around 535 nm contributed positively to PC2 and the wavelengths between 750 and 840 nm contributed negatively (Figure 4a). PC3 was weakly correlated with BD600 (Figure 3c, $\rho = 0.60$). Wavelengths 550–650 nm contributed negatively and 750–840 nm wavelengths contributed positively to PC3 (Figure 4a). PC4 was negatively correlated with S7584 (Figure 3d) and the spectral maximum ($\rho = -0.85$ and -0.72 , respectively). The areas around 560 nm and past 800 nm contributed negatively to PC4, whereas the 600–725 nm region contributed positively (Figure 4a). PC3 and PC4 explained 0.42% and 0.23% of the variance, respectively. The loading plots for PC5 through PC8 show a significant increase in volatility below 500 nm and an increase in noise overall (Figure 4b). Cumulatively explaining less than 0.12% of the variance of the passive spectral data set, PCs past PC4 were not found to meaningfully relate to any spectral features in the data set. Figure 5 shows PC2 plotted against PC1 and PC4 plotted against PC3—as expected, the PCs are not correlated with one another. Figure 6 shows representative ChemCam spectra for maximum and minimum values for PCs 1–4.

4.2. Passive Spectral Parameters

There are variations in the calculated passive spectral parameters over Curiosity's traverse (Table 2), expanded here from previous work (e.g., Fraeman et al., 2020; Johnson et al., 2015, 2016). BD535 increases until the

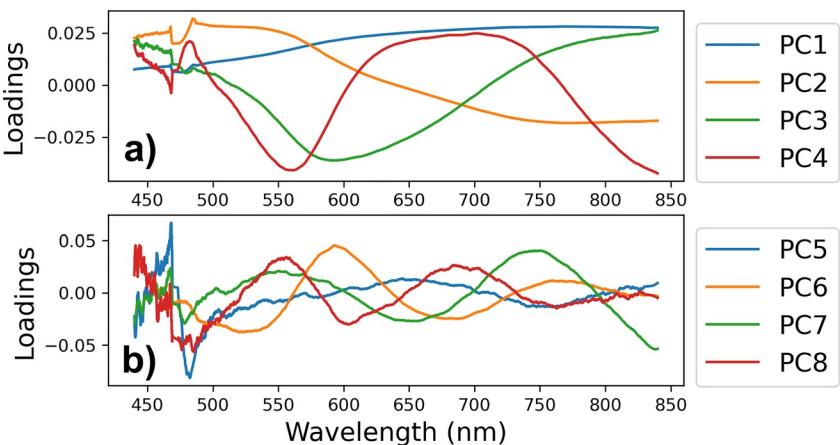


Figure 4. The principal component (PC) loadings plotted against wavelength for (a) PCs 1–4 and (b) PCs 5–8. The greater the loading value is above zero for a given wavelength and a given PC, the more that wavelength range positively contributes to that PC. The more negative the loading is, the more that wavelength range negatively contributes to that PC. A loading near zero indicates that region is not important for that given PC.

boundary between Sutton Island and Blunts Point (sol 1690), where it then decreases (Figure 7c). This is mirrored by S7584, which broadly decreases until sol 1690 where it increases briefly (Figure 7a), and it is also mirrored by the spectral maximum which peaks around sol 1690 (Figure 7b). Another rapid decrease in BD535 is seen in Jura, followed by a more gradual decrease during the rest of the traverse. There is a small peak in BD535 near the area in the Vera Rubin ridge (VRR) with the deepest BD860 absorptions seen by CRISM from orbit (sol ~2004) (Fraeman et al., 2020). BD600, which is related to the strength of the short wavelength ferric oxide absorption edge (Johnson et al., 2015; Morris et al., 1985), largely stays between –0.05 and 0.15, except for the Jura member where it dips to as low as –0.28 (Figure 7d). Negative band depth values indicate concavity in a spectrum, not an absorption. Many of the passive spectral parameters are correlated with each other (Figure 8).

4.3. Spectral End-Members

Results from the above PCA show focusing on trends in BD535 and S7584 is a good way to visualize the spectral variability of the data set. Plotting these two spectral parameters on a scatter plot reveals five distinct classes of spectra. These classes were identified based on their position along or deviation from the main trend (the negative correlation between BD535 and S7584). Combined large BD535 values and negative NIR slopes (S7584) are

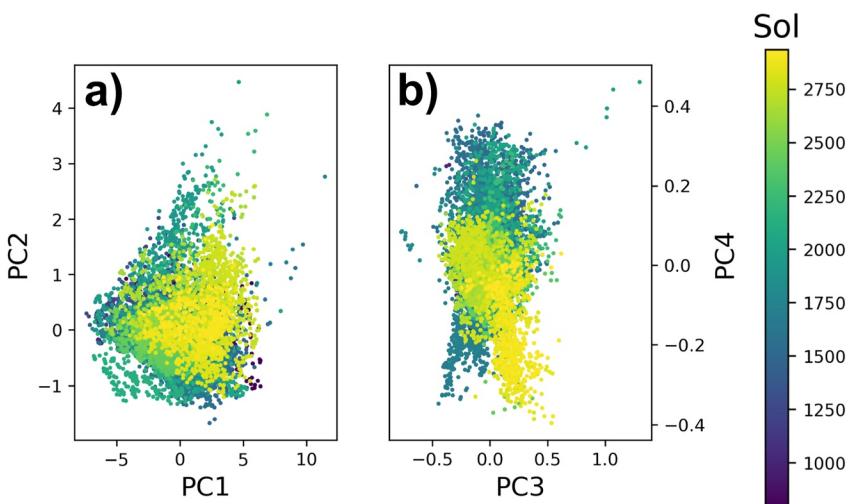


Figure 5. (a) PC2 plotted against PC1 and (b) PC4 plotted against PC3. Colored by sol number.

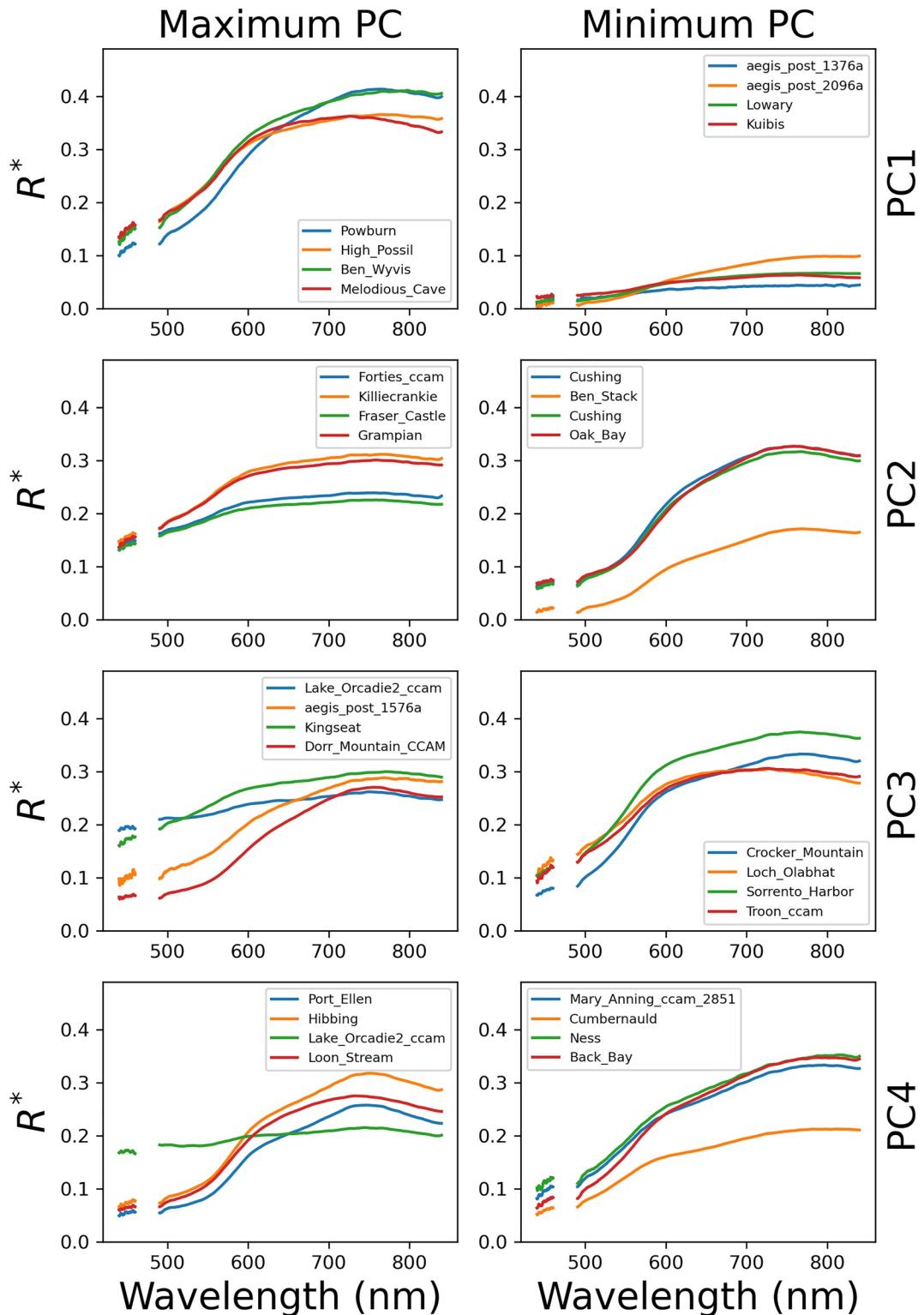


Figure 6. ChemCam passive spectra randomly chosen within the 150 observations with maximum (left) and minimum (right) values of principal components (PCs) 1–4. Data near the violet and near-infrared detector edges (460–490 nm) have low signal-to-noise ratio (SNR) and have been removed for visualization purposes.

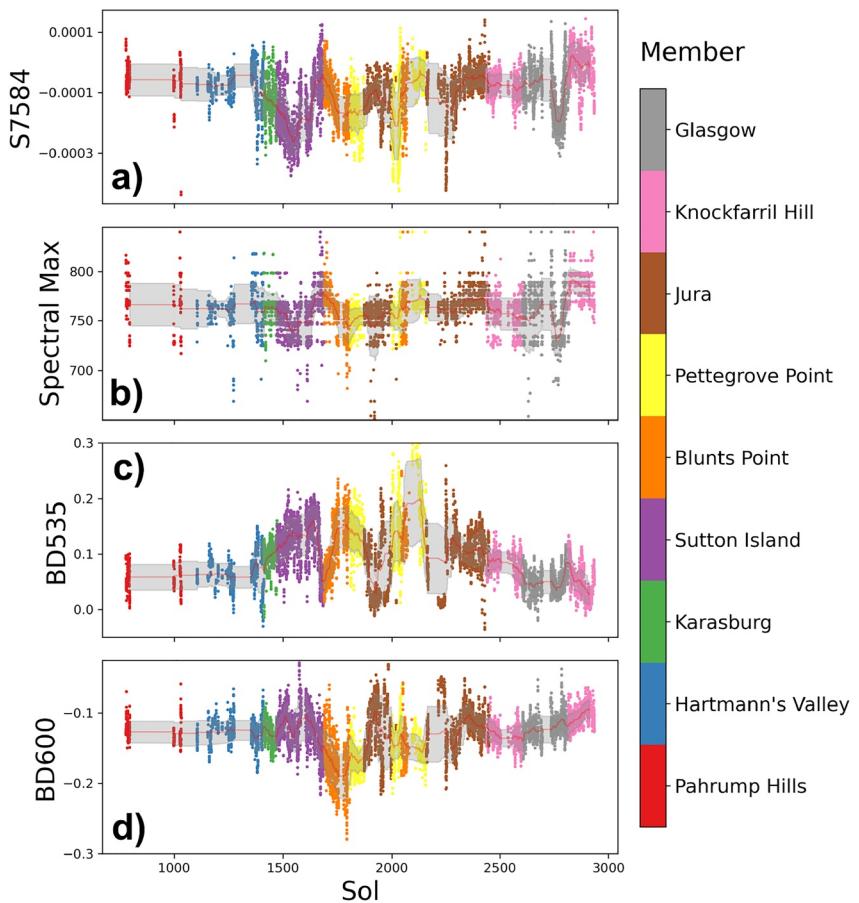


Figure 7. S7584 (a), Spectral maximum (b), BD535 (c), and BD600 (d) plotted against sol. Data are colored by geologic member. Rolling average (red line) and rolling standard deviation (transparent gray interval) of 250 observations are included.

typical of ferric oxides (e.g., Fraeman et al., 2020); an example of a ChemCam target with these features (“Conan Mains,” point U) is shown in Figure 9. “Ness,” Point X (Figure 9), is a target with no near-infrared (NIR) slope and near-zero BD535. “Fishnish,” Point Y (Figure 9), is a target representative of many measurements from the

	Sol	PC1	PC2	PC3	PC4	BD535	BD600	S7584	R6744	R6084	Spectral Maximum	Avg. Relative Reflectance
Sol	1	0.09	0.14	0.15	-0.26	-0.27	0.19	0.26	0.01	-0.08	0.17	0.1
PC1	0.09	1	-0.09	-0.04	0.01	-0.16	0.16	-0.13	0.12	-0.02	0.09	0.99
PC2	0.14	-0.09	1	-0.14	-0.02	-0.74	0.26	0.02	-0.91	0.81	-0.25	0.01
PC3	0.15	-0.04	-0.14	1	0.01	0.07	0.6	0.25	-0.09	-0.53	0.35	-0.04
PC4	-0.26	0.01	-0.02	0.01	1	0.5	0	-0.84	-0.11	0.22	-0.72	0.01
BD535	-0.27	-0.16	-0.74	0.07	0.5	1	-0.42	-0.4	0.62	-0.5	-0.16	-0.24
BD600	0.19	0.16	0.26	0.6	0	-0.42	1	0.16	-0.35	-0.11	0.1	0.2
S7584	0.26	-0.13	0.02	0.25	-0.84	-0.4	0.16	1	0.04	-0.33	0.77	-0.12
R6744	0.01	0.12	-0.91	-0.09	-0.11	0.62	-0.35	0.04	1	-0.69	0.25	0.03
R6084	-0.08	-0.02	0.81	-0.53	0.22	-0.5	-0.11	-0.33	-0.69	1	-0.54	0.06
Spectral Maximum	0.17	0.09	-0.25	0.35	-0.72	-0.16	0.1	0.77	0.25	-0.54	1	0.06
Avg. Relative Reflectance	0.1	0.99	0.01	-0.04	0.01	-0.24	0.2	-0.12	0.03	0.06	0.06	1

Figure 8. A Spearman’s ρ Correlation Matrix of ChemCam passive spectra.

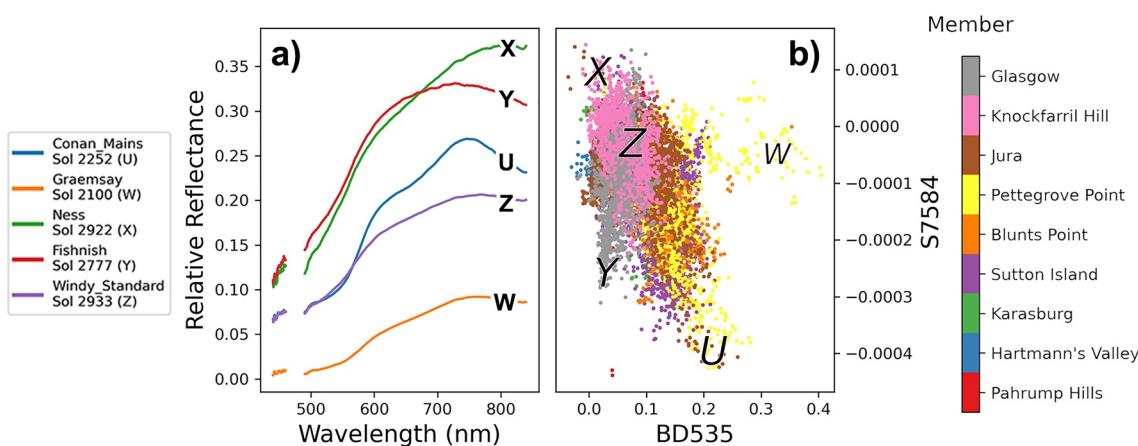


Figure 9. (a) Relative reflectance plotted against wavelength for five end-member spectra. (b) S7584 plotted against BD535, colored by geologic member, for all passive ChemCam observations in the data set. Letters U–Z in panel (b) correspond to the spectra shown in panel (a), which are averages for a given target. Low signal-to-noise ratio (SNR) data around the violet/near-infrared detector gap (~ 460 – 490 nm) have been removed.

Glasgow member that have large NIR slopes but weak to near-zero BD535. “Windy Standard” Point Z (Figure 9) is spectrally similar to the average Murray and Carolyn Shoemaker formation bedrock, with BD535 of ~ 0.08 and S7584 between 0 and -0.0001 .

Some spectra were affected by a dust storm. “Graemsay,” Point W (Figure 9), is a target with very strong BD535, low average relative reflectance, and anomalously high R6744 and is characteristic of ChemCam passive spectral observations taken during the 2018 global dust storm. The dust storm significantly increased dust optical depth at 880 nm (τ) as measured by the Mastcam instrument on Curiosity, reaching a maximum of $\tau = 8.5$ around sol 2100 (Guzewich et al., 2019). This resulted in poorly calibrated ChemCam relative reflectance observations with unusually high atmospheric dust contamination, in particular low average relative reflectance, very high band depth at 535 nm, and a ratio of the reflectance at 670–440 nm between 10 and 30. There are 44 of these dust storm points representing 15 distinct targets between sol 2093 and 2130.

4.4. Passive Spectra Compared to LIBS Data

Correlations between passive spectral properties and elemental abundances measured by LIBS were explored to search for additional insight into the sources of spectral variability and compositional trends in Mt. Sharp bedrock. Of particular interest was any relationship (or lack thereof) between spectral parameters and FeO_T , since the VNIR spectral range is sensitive to charge-transfer and crystal-field absorptions most commonly associated with iron-bearing minerals. Correlations between spectral parameters and other elements could also highlight compositionally distinct regions.

When considering all Mt. Sharp group bedrock targets, no correlations between any of the major or trace oxides measured by LIBS and passive spectral features were found (Figure 10). This indicates there is no evidence

	Sol	PC1	PC2	PC3	PC4	BD535	BD600	S7584	R6744	R6084	Spectral Maximum	Avg. Relative Reflectance
FeO_T	-0.12	-0.24	-0.03	-0.04	0.15	0.17	-0.14	-0.13	-0.01	0.07	-0.17	-0.24
MgO	0.17	-0.02	-0.19	0.14	-0.22	-0.04	0.14	0.2	0.17	-0.28	0.22	-0.04
SiO_2	0.23	-0.01	-0.11	0.16	0.06	0.09	0.13	0.07	0.12	-0.2	0.04	-0.02
K_2O	0.15	-0.16	-0.05	0.12	0.15	0.18	0.04	-0.04	0.03	-0.09	-0.08	-0.16
Al_2O_3	-0.02	0.07	-0.06	-0.01	0.04	0.04	0.06	0.03	0.08	-0.05	0.01	0.07
CaO	-0.17	0.14	0.24	-0.24	-0.07	-0.22	-0.12	0	-0.18	0.3	-0.03	0.16
Na_2O	0	-0.03	0.1	0.03	0.02	-0.06	0.1	0.07	-0.08	0.06	-0.03	-0.02
TiO_2	0.04	-0.08	0.04	0.07	0.14	0.03	0.08	-0.06	-0.04	0.04	-0.12	-0.07
MnO	-0.07	0.07	0.01	-0.11	-0.36	-0.18	-0.13	0.2	0.01	0.01	0.23	0.06

Figure 10. A Spearman’s ρ Correlation Matrix of ChemCam passive and Laser Induced Breakdown Spectroscopy Data.

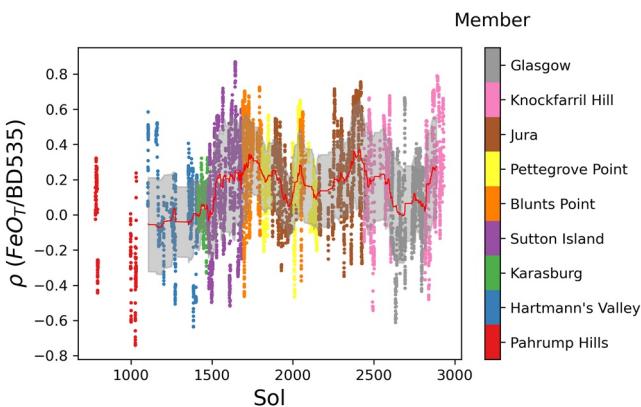


Figure 11. A rolling Spearman's correlation coefficient (ρ) of FeO_T and BD535 with a window of 50 points. A rolling average of these data over 500 observations is plotted in red with a rolling standard deviation in transparent gray.

of regions of Curiosity's traverse where iron was added via the oxidation of ferrous bearing fluids and emphasizes the complicating role effects such as grain size and mixtures can play in passive spectral observations. Ferric related spectral parameters such as PC2 and BD535 did not have any correlation with the iron oxide totals (FeO_T) from LIBS observations ($\rho = -0.03$ and 0.17, respectively, Figure 10); however, when viewed over the entire traverse, there were weak correlations in a subset of rock targets near the transition between the Sutton Island and Blunts Point stratigraphic members (Figure 11). There were also weak correlations ($\rho \approx -0.5$) between PC4 and high magnesium targets (Figure 12a) in the Sutton Island-Blunts Point transition ($\sim\text{sol} 1690$), as well as in the Knockfarril Hill member. Examination of spectra of high MgO targets in both of these regions shows they have weak BD535 and shallow S7584 (Point X, Figures 9 and 13). In these two same stratigraphic intervals, correlations between PC4 and high MnO targets were even more apparent (Figure 12b). Targets that were examined around sol 1690 (near the Sutton Island—Blunts Point transition) have very low PC4 and high weight percent MnO, whereas the surrounding rocks have both much higher PC4 and low MnO values (Figure 12b).

Although not evident in the bulk measurements, there is some relationship between PC4 and high magnesium targets (Figure 12a). This is particularly obvious around the Sutton Island-Blunts Point transition ($\sim\text{sol} 1690$) and in Knockfarril Hill (an example spectrum is shown as point X in Figure 9). This appears to stem from the fact that high MgO targets have shallow BD535 and little S7584 (Figure 13). The same is true, and even more apparent, of high MnO targets. The sols immediately around sol 1690 have very low PC4 and weight percent MnO, whereas the surroundings have much higher PC4 and MnO values (Figure 12b).

Somewhat weaker correlations ($0.4 < \rho < 0.7$) between spectral parameters and LIBS chemistry when examined by individual stratigraphic member include:

- In Sutton Island, SiO_2 is negatively correlated with PC2 ($\rho = -0.44$) and MnO is correlated with PC4 ($\rho = -0.49$).
- In Blunts Point, all the major oxides are correlated with R6744 (and by extension PC2). R6744 is correlated with FeO_T , MgO , SiO_2 , K_2O , Al_2O_3 , CaO , TiO_2 , and Na_2O ($\rho = 0.52$, 0.41, 0.65, 0.63, 0.59, -0.60, 0.55, and 0.57, respectively). BD535 is correlated with K_2O and MnO ($\rho = 0.44$ and -0.55, respectively). MnO and PC4 are also correlated ($\rho = -0.44$).
- In Knockfarril Hill, PC3 is correlated with MgO and MnO ($\rho = 0.58$ and 0.47, respectively). PC4 is correlated with FeO_T , MgO , K_2O , and MnO ($\rho = 0.49$, -0.70, 0.45, and -0.65, respectively). BD535 is correlated with FeO_T , MgO , SiO_2 , K_2O , and MnO ($\rho = 0.40$, -0.59, 0.45, 0.62, and -0.68, respectively).
- In Glasgow, S7584 is correlated with K_2O and MnO ($\rho = -0.40$ and 0.50, respectively).

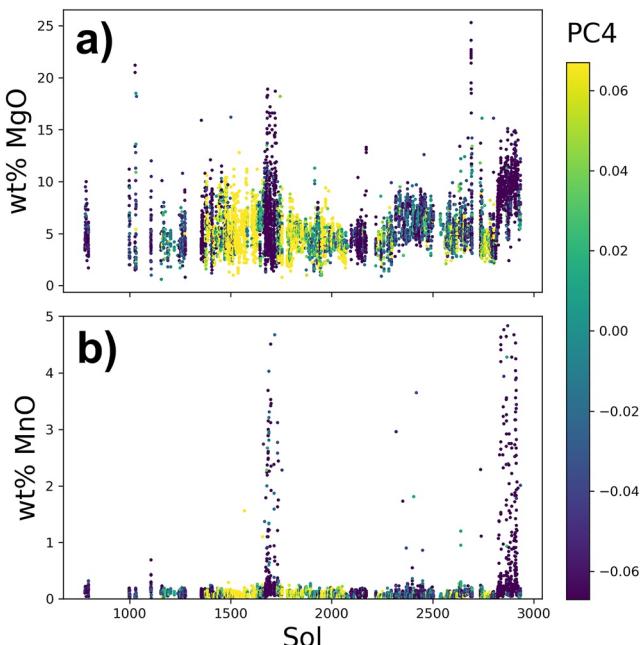


Figure 12. Weight percent of (a) MgO and (b) MnO plotted against sol. Colored by PC4.

4.5. Comparison to CheMin Data

Although collected much more rarely than ChemCam LIBS data, colocated CheMin mineralogical data may provide additional insight into the source(s) of the spectral variability in the Mount Sharp group rocks. Wellington et al. (2017) found correlations between CheMin analyses and Mastcam multispectral observations of drill tailings that suggested (a) the 800 nm spectral peak and 930 nm minimum in Yellowknife Bay (a Bradbury Group target) was derived from Fe-bearing phyllosilicates and pyroxenes, and (b) the 527 nm absorption in both Mastcam and ChemCam spectral data of Pahrump Hills target was consistent with the presence of crystalline hematite. Jacob et al. (2020) similarly examined CheMin data with coordinated

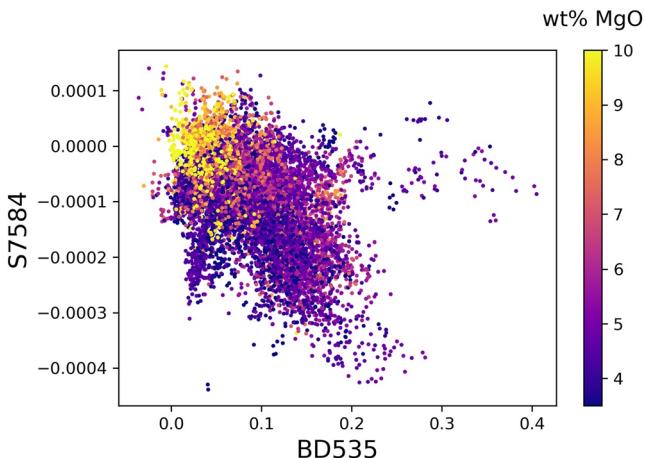


Figure 13. S7584 plotted against BD535. The points are colored by weight percent MgO, showing that high MgO correlates with low BD535 and high S7584. Outlying points at the right side of the plot near S7584 ~0 are due to poor calibration during the global dust storm.

Table 3
Average BD535 and S7584 Parameter Values From ChemCam Passive Spectra for Targets With Both CheMin and ChemCam Data in the Murray and Carolyn Shoemaker Formations

Drill name	ChemCam target name	Sol	BD535	S7584 (10 ⁻⁴)
Marimba	Marimba	1418	0.107	-0.43
Quela	Quela_DRT_ccam ^a	1456	0.091	-0.64
Sebina	Sebina_ccam	1492	0.125	-1.95
Duluth	Duluth_ccam	2053	0.126	-0.65
Highfield	Rosebrae ^a	2227	0.008	-1.20
Rock Hall	Rock_Hall_ccam_1	2257	0.114	-1.62
	Rock_Hall_ccam_2	2257	0.125	-2.06
	Rock_Hall_ccam_3	2257	0.115	-2.04
	Rock_Hall_ccam_4	2259	0.107	-1.08
Aberlady	Aberlady_ccam	2367	0.089	-0.71
Kilmarie	Aberlady_ccam ^b	2367	0.089	-0.71
Glen Etive 1	Glen_Etive_1_ccam	2482	0.097	-0.72
Hutton	Hutton_ccam	2666	0.020	-0.85
	Hutton2_ccam		0.043	-0.31
Glasgow	Glasgow_2_ccam ^a	2753	0.071	-0.49
	Canongate ^a		0.040	-1.38
Mary Anning	Mary_Annинг_ccam	2831	0.054	0.73
Mary Anning 3	Mary_Annинг_3_ccam	2869	0.03	0.26
Groken	Groken_ccam	2906	0.022	0.27

Note. Stoer was not included as it was in a period of high optical tau (the 2018 global dust storm).

^aQuela, Highfield, and Glasgow did not have ChemCam data from a Dust Removal Tool (DRT) surface. ^bAberlady_ccam was used for both the Aberlady and Kilmarie drills as they are very close to one another.

Mastcam multispectral observations of drill tailings and hypothesized that variations in the 860 nm absorption feature were the result of a combination of variations in ferric phyllosilicate abundance, variations in clinopyroxene abundance, and the presence of red crystalline hematite.

Fourteen targets measured by CheMin in the Murray or Carolyn Shoemaker formation over the sol range covered in this analysis have both passive and LIBS data collected before drilling (Tables 3 and 4).

Table 3 lists two spectral parameters from ChemCam passive data, BD535 and S7584 (Table 2), related to the presence of iron bearing minerals. Three of these 14 targets were not brushed by the Dust Removal Tool (DRT). Even though the LIBS observations that are acquired before the passive spectra are often effective at clearing dust, the difference between DRT and non-DRT targets is still noted here due to possible differences in the effectiveness of dust clearing between the two techniques. Dust can increase reflectance at longer wavelengths and can also reduce the depth of absorption features (Rice et al., 2022). Table 4 lists the abundance of ferric materials inferred from CheMin data in these targets. Hematite and total ferric phase weight percent values in Table 4 are renormalized to 100% crystalline (i.e., without the amorphous components). Although there was evidence that many of the phyllosilicates in Gale Crater also have some amount of Fe³⁺, they contain variable amounts of Fe²⁺ versus Fe³⁺ in the octahedral sites, so were excluded in this comparison (Tu et al., 2021).

Highfield had a higher abundance of hematite than would be expected based on its weak 535 nm absorption and lack of downturn from 750 to 840 nm. This was interpreted to suggest that hematite in that sample was coarse-grained “gray hematite” (Jacob et al., 2020; Rampe, Bristow, et al., 2020). For sufficiently large hematite particles ($>\sim 3\text{--}5\ \mu\text{m}$), the ferric absorption edge is weak or not present, meaning it is approximately spectrally neutral over visible wavelengths, imparting a black to gray color (Catling & Moore, 2003; Lane et al., 2002; Morris et al., 2020). When Highfield is not included, there was a strong correlation ($\rho = 0.75$) between BD535 and weight percent of total crystalline ferric phases as reported by CheMin (Figures 14 and 15a). This is consistent with findings from Mastcam multispectral data (Jacob et al., 2020; Rice et al., 2022; Wellington et al., 2017). S7584 was correlated with crystalline ferric phases ($\rho = -0.61$, Figure 15b) and with weight percent amorphous FeO_T ($\rho = 0.66$). The target with the highest average BD535 and steepest NIR slope (Sebina_ccam) corresponded to the sample with the most total crystalline ferric phases measured by CheMin (23 wt%). The target with the lowest weight percent ferric phases (Groken) was also the ChemCam target with the lowest average BD535 and very little S7584. Importantly, all targets with ChemCam observed absorptions attributed to ferric iron contained ferric phases measured by CheMin. This indicates that the total abundance of crystalline ferric phases was a major source of variation in ChemCam passive reflectance spectra, with weight percent amorphous FeO_T also playing a role. As demonstrated by Highfield, the grain size of the ferric phases can also affect passive reflectance spectra.

5. Discussion

5.1. Summary of Spectral Variability in ChemCam Passive Spectra

PCA demonstrates that, after average relative reflectance, the biggest driver of variability in ChemCam passive spectra of Mt. Sharp group rocks are changes in ferric-related spectral absorptions. PC2 explains 6.61% of the variance of the data set, and it is correlated with the depth of the 535 nm

Table 4

CheMin Data for Targets in the Murray and Carolyn Shoemaker Formation With Both CheMin and ChemCam Data

Drill name	Crystalline hematite (wt%)	Total crystalline ferric phases (wt%)	FeO _T in amorphous component (wt%)	Hematite crystallite size (nm)
Marimba	16.4 ± 2.1	17.9 ± 2.6	29.7	38.4
Quela	20.0 ± 1.5	21.4 ± 2.1	20.4	25.1
Sebina	20.4 ± 1.7	23.0 ± 2.3	18.8	26.8
Duluth	13.0 ± 0.8	13.0 ± 0.8	26.1	17.9
Highfield	20.2 ± 1.3	20.2 ± 1.3	7.4	30.7
Rock Hall	5.4 ± 0.4	21.0 ± 2.2	17.5	39.4
Aberlady	5.5 ± 1.4	5.5 ± 1.4	15.2	26.8
Kilmarie	3.8 ± 1.0	3.8 ± 1.0	12.4	No data
Glen Etive 1	7.0 ± 2.5	7.0 ± 2.5	14.4	19.7
Hutton	4.8 ± 1.2	4.8 ± 1.2	8.4	28.1
Glasgow	13.4 ± 3.1	13.4 ± 3.1	12.3	16.2
Mary Anning	2.5 ± 1.6	2.5 ± 1.6	21.4	15.6
Mary Anning 3	1.9 ± 0.5	1.9 ± 0.5	21.2	26.8
Groken	0.0	0.0	20.3	31.3

Note. Total crystalline ferric phases are CheMin-derived hematite, jarosite, and akaganeite abundances added together; magnetite is not included as it does not have ferric spectral expressions at 535 nm. CheMin abundances data were obtained from the Planetary Data System (Vaniman, 2022). FeO_T in amorphous component is normalized to 100% amorphous. FeO_T in amorphous component and hematite crystallite size were obtained from Achilles et al. (2020), Rampe, Blake, et al. (2020), Rampe, Bristow, et al. (2020), and Thorpe et al. (2022).

absorption (Fe³⁺ electronic pair transition) (Figure 3b), visible slope or “redness” (R6744), and near infrared slope (R6084). PC3, with 0.42% of the variance, is loosely correlated with BD600, which is related to the strength of the ferric oxide absorption edge (Figure 3c), and PC4 (0.22% of the variance) is correlated with the slope from 750 to 840 nm, which is also related to electron transitions in ferric minerals (Figure 3d). Loading plots for PCs 5–8 show a large increase in noise below 500 nm (Figure 4b), and PCs 5–8 were not found to meaningfully relate to any spectral parameters.

Calculated passive spectral parameters varied significantly across the rover traverse. BD535 broadly increased until Pettegrove Point, near the VRR, where it decreased toward Glasgow and Knockfarril Hill. There was also a significant decrease in BD535 near sol 1690, which was mirrored by an increase in the NIR slope and the spectral maximum approaching 840 nm (see Section 5.3). A small peak in BD535 occurred near the area in the VRR with the strongest BD860 absorptions seen by CRISM from orbit (sol ~2004), although it was only moderately higher than other parts of the traverse (Fraeman et al., 2020).

The depth of the 535 nm absorption (~PC2) and S7584 (~PC4) cannot be used as a direct proxy for the amount of iron oxides or ferric materials in a sample; factors such as mineral grain sizes and mineral mixtures also have been shown to affect the strength of these features in Mt. Sharp group rocks (Jacob et al., 2020; Wellington et al., 2017). However, the 14 samples of Murray and Carolyn Shoemaker formation bedrock analyzed by CheMin that had corresponding ChemCam passive observations did show a correlation between the strength of these absorption features and total ferric phases in the sample (Figure 15), demonstrating that the abundance of ferric phases is an important driver in the presence and depth of these absorptions. The target with the highest abundance of ferric phases as measured by CheMin, Sebina, had a deep 535 nm absorption and strong NIR slope, while the target with the lowest abundance of ferric phases, Groken, had very little BD535 and flat NIR slopes (Figure 15).

These findings are consistent with complementary Curiosity data sets. Spectral variations in Mastcam multispectral data are dominated by spectral differences that are attributed to hematite and other oxides (Jacob et al., 2020; Rice et al., 2022). Rice et al. (2022) identified nine distinct classes of Mastcam rock spectra from sols 0–2302, some of which are broadly similar to the ChemCam passive spectral end-members identified in this work. For example, Class “U” (Figures 9 and 16) is analogous to Class 4 (Hexriver) from Rice et al. (2022), both being consistent with red fine-grained hematite. Although a fewer number of samples were analyzed, CheMin analyses of drilled samples from the Murray formation varied in the amount and types of oxidized phases they contained (Bristow et al., 2018; Rampe, Blake, et al., 2020).

5.2. Spectrally Unique Areas

Figure 16 plots S7584 versus BD535 (correlated with PC4 and PC2, respectively), which reveals trends and spectrally unique regions in Mt. Sharp. Rocks in the Pettegrove Point member and portions of the Jura member associated with the Vera Rubin ridge have the highest combined BD535 and S7584 (class “U” in Figures 9 and 16), as well as the lowest BD535 and S7584 (class “X”). The unique spectral properties in this area have been explored in detail (Fraeman et al., 2020; Horgan et al., 2020; Jacob et al., 2020; L’Haridon et al., 2020) and a leading hypothesis is hematite of variable grain sizes formed by diagenesis, possibly in association with the destruction of clay minerals by silica-poor brines (Bristow et al., 2021). Two other groups of spectrally distinct ChemCam passive

	BD535	S7584	Hematite	Ferric Phases	Amorphous FeO _T	Hematite size
BD535	1	-0.37	0.68	0.75	0.34	-0.03
S7584	-0.37	1	-0.48	-0.61	0.66	-0.14
Hematite	0.68	-0.48	1	0.92	0.08	-0.16
Ferric Phases	0.75	-0.61	0.92	1	0.04	0.07
Amorphous FeO _T	0.34	0.66	0.08	0.04	1	-0.03
Hematite size	-0.03	-0.14	-0.16	0.07	-0.03	1

Figure 14. A Spearman’s ρ Correlation Matrix of ChemCam passive and colocated CheMin mineralogy data. Highfield was not included in this analysis.

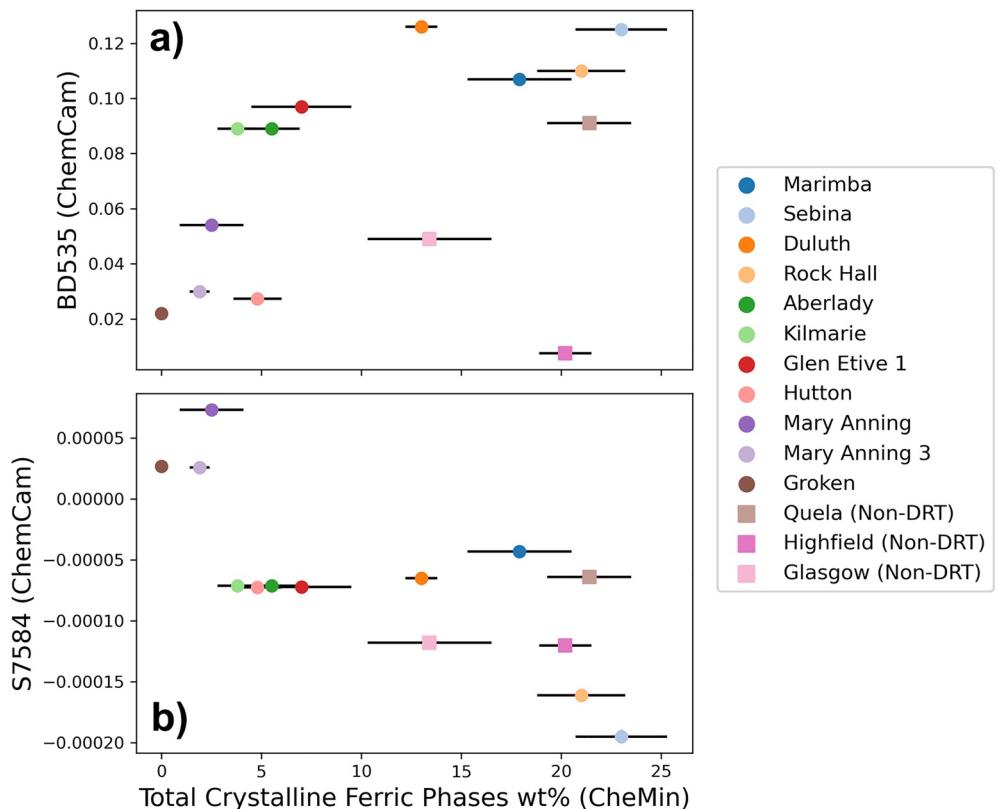


Figure 15. (a) BD535 and (b) S7584 derived from ChemCam passive observations versus total crystalline ferric phases (hematite, jarosite, and akaganeite) from CheMin for all Mt. Sharp group drill holes for which a corresponding ChemCam observation. Targets marked with a square represent observations not taken on a Dust Removal Tool surface.

observations include those taken in the Glasgow member and during the 2018 global dust storm. Each of these are discussed below.

5.2.1. Glasgow Member and the Hutton Interval

The transition between the Knockfarril Hill and Glasgow members is spectrally unique. Most Knockfarril Hill member targets have spectral features similar to average Mt. Sharp group bedrock (small BD535 and S7584 values), whereas many Glasgow targets have low BD535 and strongly negative NIR slopes (point Y in Figures 9 and 16). The spectral difference could be the result of average Murray/Carolyn Shoemaker bedrock mixing with a new spectral end-member with less abundance or coarser grained ferric phases. Interestingly, analyses of sedimentary structures in this area showed a change in lithology that marked a significant transition from dominantly lacustrine to fluvial environments (Caravaca et al., 2022; Fedo et al., 2022). The concurrent changes in lithology and spectral properties could therefore be indicative of compositional variations that either reflect a shift in the primary depositional environment and/or different styles of diagenesis in this area.

A shift toward stronger S7584 but still shallow BD535 occurs around sol 2750–2800, at an area referred to as the Hutton interval. This interval occurs in the Glasgow member below the Siccar Point unconformity, and it is also associated with a color change in Mastcam color images, as well as a unique CheMin (Dehouck et al., 2022; Rudolph et al., 2022; Thompson et al., 2022; Thorpe et al., 2022). Specifically, the Hutton interval in the Glasgow member is characterized by a decrease in chemical index of alteration values, localized enrichments and depletions in mobile elements, and a significant amount of cristobalite and opal-CT (Dehouck et al., 2022; O'Connell-Cooper et al., 2022; Thorpe et al., 2022).

There are two end-member hypotheses to explain the unique composition of the Hutton interval: (a) there was a significant shift in the combination of alteration conditions and the nature of the sediment source or (b) this interval is a region of enhanced diagenesis related to the Siccar Point unconformity (e.g., Dehouck et al., 2022). Each scenario predicts a different regional distribution of Hutton interval type material with respect to the Siccar

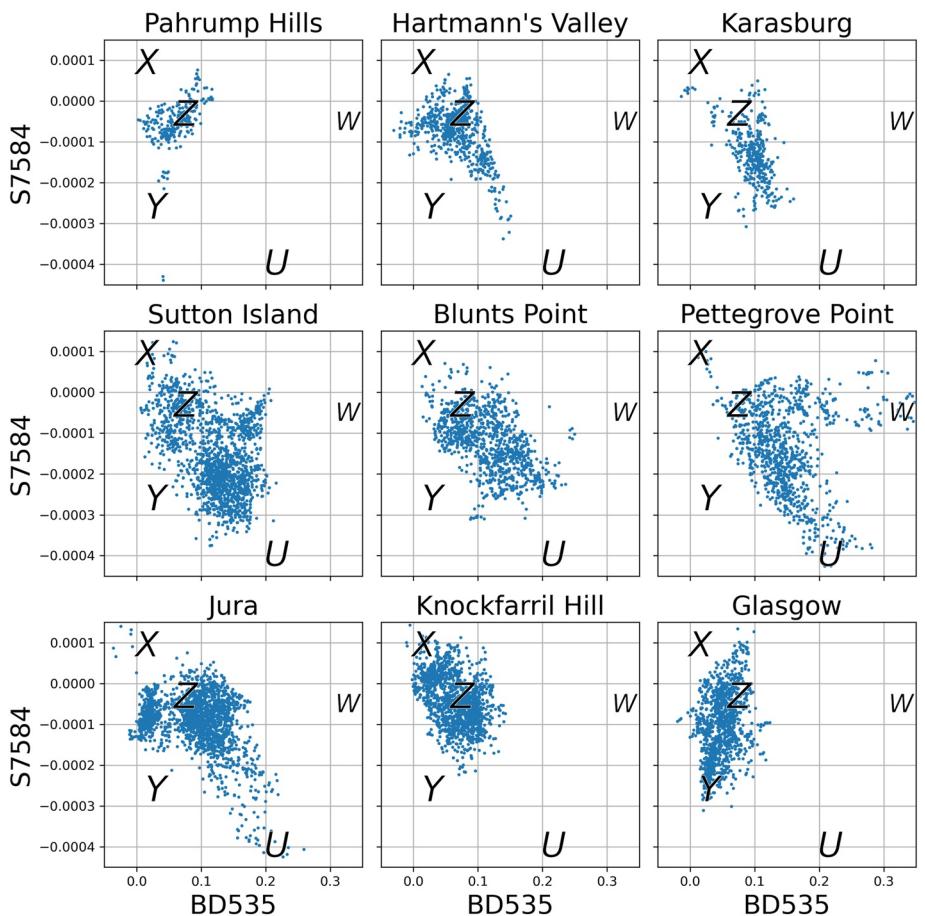


Figure 16. S7584 plotted against BD535 in each geologic member of the Mt. Sharp group. Spectral classes “U” through “Z” from Figure 9 are also plotted for context.

Point unconformity, which Curiosity will have a chance to test to if it revisits the unconformity at a higher elevation. If the Hutton interval is related to the diagenesis along the unconformity, rocks with similar compositional characteristics will reappear. If the interval is related to depositional environments, the rocks near the Siccar Point unconformity to the south may be different. The discovery that the Hutton interval unconformity has unique spectral properties will provide additional criteria to test these hypotheses from Curiosity remote sensing data (whose acquisition is less resource intensive than drill sample collection for CheMin).

5.2.2. Targets Acquired During High Tau

ChemCam observations taken during the 2018 global dust storm were readily identified by their passive spectral features (class “W” in Figure 9), in particular average relative reflectance below 0.085, BD535 above 0.3, and R6744 between 10 and 30. R6744 (the red-blue ratio) has been used as a first-order approximation for dust cover at the Mars Pathfinder landing site (Johnson et al., 2003) and is similarly useful in ChemCam passive spectra. R6744 values above 10 occur exclusively during the 2018 dust storm between sol 2093 and 2130. We include dust storm observations here (44 measurements of 15 distinct targets) for completeness but note that spectral parameter correlations for these observations should be considered separately. This is evidenced by their very high BD535 but weak S7584 values (e.g., Figure 13), which are consistent with shadowed targets (Johnson et al., 2015).

5.3. Comparison Between Spectral and Chemical Properties of Bedrock Targets

Active LIBS chemical data collected from the same locations as passive spectral data provide a unique opportunity to directly compare chemical and spectral properties of Mt. Sharp bedrock.

Weight percent FeO_T reported by LIBS and BD535 from passive spectra are not correlated (Spearman's $\rho = 0.18$) on the scale of Curiosity's traverse or generally within any individual member. The decoupled nature of FeO_T and BD535 demonstrates that regions with strong 535 nm absorption bands, like the Vera Rubin ridge, are not associated with areas where iron was added to the host bedrock (David et al., 2020; Frydenvang et al., 2020), for example, by being carried by anoxic groundwater and subsequently precipitating at a redox interface (as proposed by Fraeman et al. (2013)).

Interestingly, there was an increase in the correlation strength between FeO_T and BD535 near the boundary of Sutton Island and Blunts Point and a small increase in Knockfarril Hill (Figure 11)—two areas that are notable for their relatively high weight percent MnO targets (Figure 12b). The presence of MnO is an indication of strongly oxidizing conditions (Lanza et al., 2016), but across the traverse there is no monotonic relationship between this potential signature of iron oxidation (the correlation coefficient of FeO_T and BD535) and weight percent MnO.

Comparison of passive relative reflectance spectra and LIBS elemental data highlighted the boundary of Sutton Island and Blunts Point (sol 1690) as an area of interest. This region was proposed to be an interval of low lake level, as indicated by the presence of highly soluble hydrated magnesium sulfates associated with the bedrock detected both in situ (Rapin et al., 2019) and from orbit (Sheppard et al., 2021). These magnesium sulfate rich bedrock targets were found to have significantly lower PC4 than the surrounding terrain (Figure 12), corresponding to near zero S7584 (Figure 7a), weak BD535 (Figure 7c), and a spectral maximum approaching 800 nm (Figure 7b). This is consistent with Mastcam observations, which suggest a significant decrease in crystalline hematite relative to the rest of the Murray formation and an increase in other iron bearing phases with band centers past the wavelength range of ChemCam (\sim 910–930 nm) such as Fe/Mg smectite, jarosite, and akaganeite (Haber et al., 2022). This compositional change is indicative of more surface exposure and a low stand environment, as described in Rapin et al. (2019). In clearly identifying this important region, PCA of passive spectra has demonstrated that it is a valuable tool for gaining additional geochemical insight from ChemCam data.

In Blunts Point, PC2 and R6744 were moderately correlated with all major oxides reported by LIBS (R6744 had positive correlations with FeO_T , MgO , SiO_2 , K_2O , Al_2O_3 , Na_2O , and TiO_2 and negative correlations with CaO) (Section 4.4). This was not seen in any other stratigraphic member in this data set and is likely the result of Ca sulfate cements that were previously identified in this region by ChemCam (M. A. Nellessen et al., 2019). Abundances of 10–25 wt% CaO consistent across a given target is characteristic of these cements (M. Nellessen et al., 2018). This is in contrast to vein observations (Figure 2) showing pure Ca sulfates (e.g., lacking any silicate component and displaying higher Ca and S signatures). These cements are likely formed by Ca sulfate precipitation into the pore space prior to lithification of the sandstone. The cements thus indicate a change in the depositional environment, such as a change in the deposition rate, or more likely, a shoreline environment in which evaporation-dominated areas are separated from the main body of the lake (e.g., Rapin et al., 2019).

6. Conclusions

Passive relative reflectance spectra of bedrock targets taken by ChemCam in the Murray and Carolyn Shoemaker formations were analyzed using PCA, spectral parameters, and compared to their corresponding LIBS elemental abundances. PCA of ChemCam passive spectra proved useful in highlighting geochemically distinct regions of the traverse. The Blunts Point-Sutton Island transition, which contains magnesium sulfate rich targets and has been proposed as an area of low lake level by Rapin et al. (2019), was found to have zero 750–840 nm spectral slope (PC4) and weak 535 nm band depth (PC2), in agreement with Mastcam data from this interval (Haber et al., 2022). The Hutton interval (sol 2750–2800) was found to be spectrally distinct from the rest of the Mt. Sharp group, having strong 750–840 nm spectral slope slopes but little change in 535 nm band depth. This indicates either a change in alteration conditions or enhanced diagenesis in this region. Comparisons between spectral parameters and LIBS data in Blunts point also suggest influences from calcium cements. The correlation coefficient between FeO_T reported by LIBS and BD535 from passive spectra was investigated as a tool for understanding the changing oxidation conditions across Curiosity's traverse. Higher than average correlations between FeO_T and BD535 were found in the Blunts Point-Sutton Island transition and Knockfarril Hill, regions known to be rich in MnO, but this signature of oxidizing conditions was not found to rise to significance on the scale of the traverse.

Data Availability Statement

The derived data used to generate figures featured in this article are available on Mendeley Data (Manelski, 2023). The MSL ChemCam Passive Surface Spectra bundle (Johnson, 2022) was obtained from the Planetary Data System (PDS). CheMin and LIBS data were also obtained from the PDS (Vaniman, 2022; Wiens, 2022). MSL Localizations for mapping were acquired on the PDS (Deen, 2015).

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