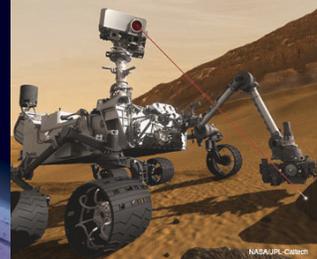


ChemCam: Chemostratigraphy by the First Mars Microprobe

Roger C. Wiens¹, Sylvestre Maurice², and the MSL Science Team

1811-5209/15/0011-0033\$2.50 DOI: 10.2113/gselements.11.1.33



An artist's conception of the ChemCam instrument aboard the Curiosity rover in operation. COURTESY NASA/JPL-CALTECH

The ChemCam laser-induced breakdown spectrometer on the rover Curiosity has provided more than 200,000 spectra from over 5000 different locations on Mars. This instrument is the first chemical microprobe on Mars and has an analytical footprint 0.3–0.6 mm in diameter. ChemCam has observed a measure of hydration in all the sedimentary materials encountered along the rover traverse in Gale Crater, indicating the ubiquity of phyllosilicates as a constituent of the analyzed sandstones, mudstones, and conglomerates. Diagenetic features, including calcium sulfate veins, millimeter-thick magnesium-rich diagenetic ridges, and manganese-rich rock surfaces, provide clues to water–rock interactions. Float clasts of coarse-grained igneous rocks are rich in alkali feldspars and some are enriched in fluorine, indicating greater magmatic evolution than expected on Mars. The identification of individual soil components has contributed to our understanding of the evolution of Martian soil. These observations have broadened our understanding of Mars as an active and once habitable planet.

KEYWORDS: Mars geochemistry, chemostratigraphy, laser-induced breakdown spectroscopy, Curiosity rover, Gale Crater

INTRODUCTION

Determining geological history from the rock record requires gathering mineralogical, compositional, and textural information over a wide range of spatial scales. On Earth, thin sections of rock samples allow the study of minerals and textures, while finer scales are routinely investigated with ion probes, electron microprobes, laser-ablation inductively coupled plasma mass spectroscopy instruments, and scanning electron microscopes. This arsenal of tools is unavailable, however, when exploring another planet. With the exception of high-resolution microscopic cameras and an atomic force microscope (Pike et al. 2011), chemical and mineralogical analyses on Mars were previously done at a scale of centimeters or larger. For example, the footprint of the alpha particle X-ray spectrometers (APXSs) on the Mars Exploration Rovers (MERs) is 3.8 cm in diameter and the miniature thermal emission spectrometer (Mini-TES) had a minimum spot size of ~8 cm in diameter (Squyres et al. 2003).

We proposed a radically new concept for the Mars Science Laboratory (MSL) rover Curiosity: an active laser experiment that would probe submillimeter scales at distances of up to 7 m from the rover (Maurice et al. 2012; Wiens et al. 2012). The ChemCam instrument suite includes the first laser-induced breakdown spectrometer used on

another planet. It is mounted on the rover's mast together with a high-resolution remote microscope imager (RMI). In deploying this instrument, the size scale for the study of Mars geochemistry shrank by a factor of 100. The novel concept is to perform submillimeter-scale chemical analyses from the rover's mast rather than at close range from the arm. ChemCam's position on the mast enables large statistical surveys and allows access to targets outside the rover arm's work zone. It avoids rover stability and slip issues, which prevent arm use in many instances. So far, ChemCam has returned from Mars more than 200,000 diagnostic spectra and over 3000 high-resolution panchromatic RMI images.

ChemCam's focused laser beam is 0.3–0.6 mm in diameter, depending on target distance. When targeted grains are much larger than the beam diameter (for example, approximately 2 mm or larger), ChemCam can analyze individual mineral grains; when the grain size is much smaller than the beam, ChemCam obtains the whole-rock composition with a single observation or with only a few observations averaged together. When the grain size is at the same scale as the beam size, the mineralogy can be deduced from trends among multiple observations, and whole-rock compositions can be determined by averaging large numbers of observations.

ChemCam's pulsed laser was designed to ablate the target material. The beam provides penetration first through the dust layer that is pervasive on the surface of Mars (Fig. 1) and then into the rock or soil, allowing studies of surface alteration. Estimates of penetration depth are based on the sizes of the craters observed in the RMI images. Sighting with the RMI allows us to locate the laser pits and to observe the spatial and textural relationships of the target locations and surrounding area at a spatial scale down to 80 μm at close range (e.g. 2 m), thus resolving grains the size of fine sand. The laser's surface-cleaning capability reveals details that would otherwise be invisible (Fig. 1D).

Laser-induced breakdown spectroscopy (LIBS) uses laser pulses that briefly provide a power density of $>10 \text{ MW/mm}^2$ to ablate target material in electronically excited states, forming a ball of plasma that lasts a few microseconds (e.g. Cremers and Radziemski 2006). The plasma emits photons at wavelengths characteristic of the electronic energy transitions of the elements present in the target material. ChemCam uses a 110 mm diameter telescope to

1 Los Alamos National Laboratory
Los Alamos, NM 87545, USA
E-mail: rwiens@lanl.gov

2 Institut de Recherche en Astrophysique et Planétologie
Toulouse, France
E-mail: Sylvestre.maurice@irap.omp.eu

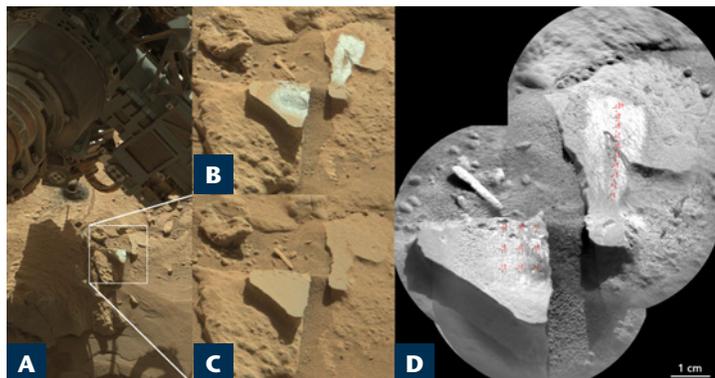


FIGURE 1 Shock waves from ChemCam's laser-produced plasma clear dust from an area around the ablation spot. **(A)** The scene near the Windjana drill hole at the Kimberley site (sol 615). The white box is ~11 cm across. **(B), (C)** ChemCam targets after and before the LIBS observations, respectively. **(D)** An RMI mosaic indicating the locations of the LIBS points (shown in red) on the two targets. These rock surfaces are rich in manganese. IMAGES COURTESY OF NASA/JPL-CALTECH

focus the laser beam and to collect light from the plasma, which is recorded using spectrometers. When calibrated, the emission-line spectra provide quantitative elemental abundances. As each laser shot probes deeper into the sample, depth profiles up to 0.5 mm in rock and greater than 1 cm in soil are achieved, and the compositions returned from the successive laser shots can be investigated. ChemCam typically provides major element (Si, Ti, Al, Fe, Mg, Ca, Na, K) relative compositions to precisions in the range of 1.0–2.0 wt% for SiO₂ in a typical basalt with 45 wt% SiO₂, and in the range of 0.2–1.0 wt% for other major elements (Blaney et al. 2014) in similar sedimentary targets. In addition to probing all the major elements, the LIBS technique as used on ChemCam is sensitive to a number of minor and trace elements, including H, Li, C, F, S, Cl, Cr, Mn, Ni, Zn, Rb, Sr, and Ba.

A spectrum from a soil target, Radcliff point #4, is shown in FIGURE 2. This target is on the edge of a rover wheel track. Transition metal elements, such as Fe and Ti, have a large number of emission lines, while some other elements at either end of the periodic table, for example, Na, K, Si, and Cl, have relatively few emission lines. In FIGURE 2, all 30 spectra obtained from this observation point are shown separately to illustrate the capability to observe compositional heterogeneity within a given observation point.

ChemCam has excellent detection limits for the alkali and alkaline earth elements. Lithium, for example, can be seen in nearly all targets, at abundances down to less than ten parts per million (FIG. 2C, INSET). The trace elements Li and Rb are sensitive to alteration and are concentrated in alkali-rich rocks, as we have seen in Gale Crater (Ollila et al. 2014). Carbonates can be detected with ChemCam, but due to interference from carbon in the atmosphere, which gets excited as part of the plasma, 4–5 wt% of the target would need to be carbonate to be identified. So far ChemCam has not observed carbonates in Gale Crater. Another important feature is the sensitivity of the LIBS to hydrogen.

Elemental compositions are quantified from ChemCam LIBS data using several calibration methods. Trace elements, such as Li, Rb, and Sr, and sometimes major elements as well, are quantified by comparing the area of a strong emission peak, observed on a target of unknown composition, to the area under the same peak for a set of calibration standards (e.g. univariate analyses; Fabre et al. 2014; Ollila et al. 2014). For major elements, the presence of multiple emission lines allows the possibility of using multivariate analytical methods, such as partial least squares, in which all the spectral channels covering multiple peaks are

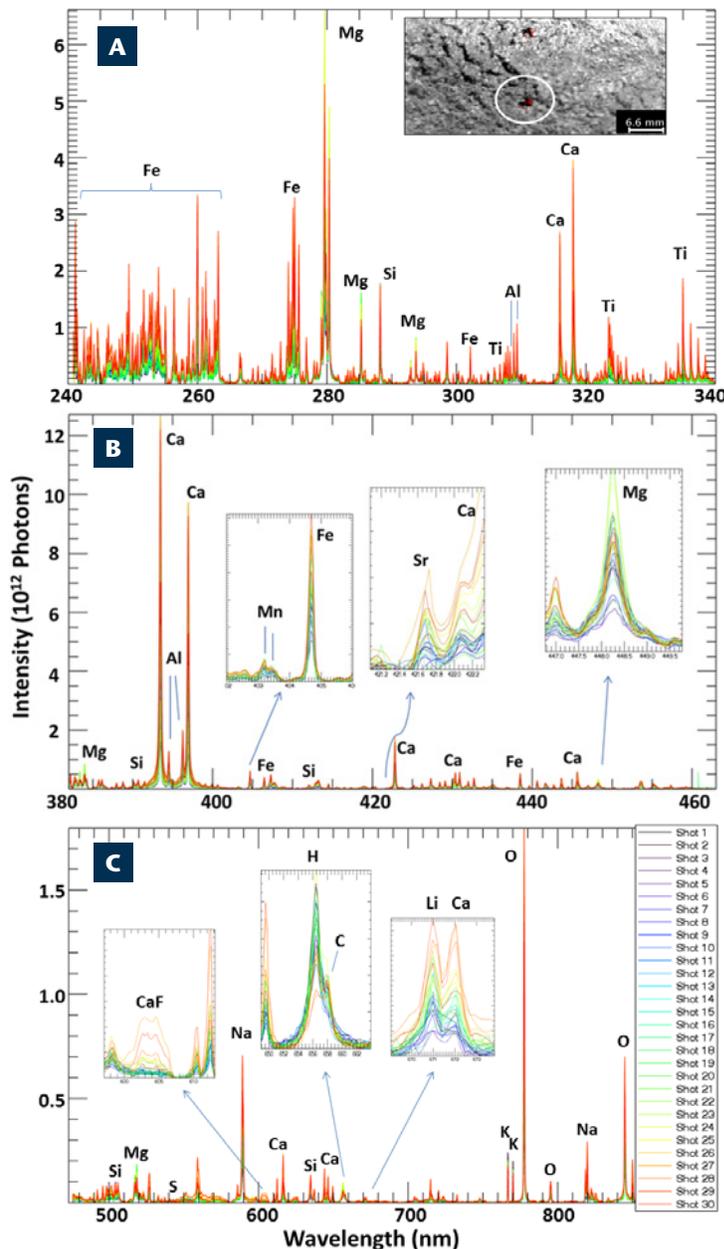


FIGURE 2 The ChemCam LIBS spectrum covers 240–906 nm with three spectrometers: **(A)** ultraviolet, **(B)** violet, and **(C)** visible and near-infrared. Shown here are individual spectra from the 30 laser shots at observation point #4 of target Radcliff (sol 676), a soil on the edge of the rover wheel track (circled in A, inset). A diversity of materials, with depth, was encountered at this observation point. Shots near the beginning and in the middle of the series were enriched in H (C, inset), which is typical of soils; shots near the middle of the series were enriched in Mg (green, panels A, C, and inset in B); and shots near the end of the series were enriched in F, Ca, Sr, and Li (C). Fluorine is observed as a broad CaF molecular emission line (C, inset); all other elements are represented by atomic and ionic emission lines.

regressed against a training set of standards. This method requires that the standards accurately cover the compositional phase space of the unknowns. ChemCam is one of the first large-scale applications of LIBS to determine the abundances of a large range of elements simultaneously, and so both of the above calibration methods are being used (Wiens et al. 2013).

The overall tactical goal of a remote-sensing rover instrument like ChemCam is to provide information about the area around the rover so that the arm-mounted and in situ instruments can be used on the most interesting samples.

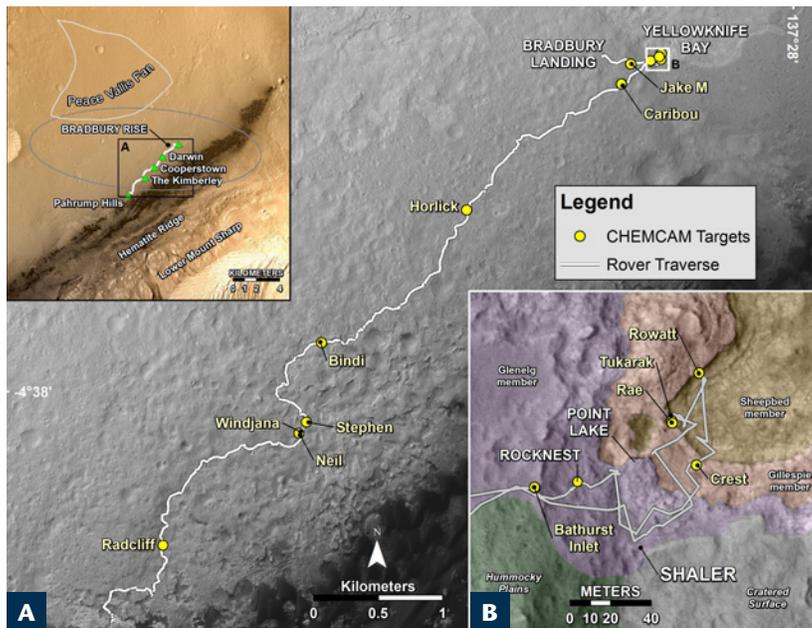


FIGURE 3 The MSL landing site in Gale Crater, a 155 km wide impact basin just south of the equator, is depicted in the upper left. The landing ellipse is sandwiched between the Peace Vallis alluvial fan and a line of sand dunes bordering the base of Mt. Sharp. The location of panel A is shown in the upper-left inset map. **(A)** The rover's traverse during the nominal mission. **(B)** The location of inset map B is shown in the top right corner of panel A and shows details from the Yellowknife Bay area. ChemCam targets mentioned in this article are indicated by yellow dots along the traverse.

In the case of ChemCam, we are also able to carry out a large amount of opportunistic science using its unique capabilities—the small analysis size, the high-resolution imaging, its sensitivity to hydrogen, and its unique ability to detect minor and trace elements. A fair amount of the science on Mars is still serendipitous because so few places have been visited.

Gale Crater was selected because, as a probable sedimentary site, it would provide greater understanding of the role of water and habitability on Mars. A number of fluvial features are observed from orbit (FIG. 3): flow channels from the crater walls and the central mound, alluvial fans, and inverted channels; in addition, some phyllosilicate mineral features have also been observed (e.g. Anderson and Bell 2010). The landed mission has clearly confirmed Gale as an important sedimentary site.

Although characterization of the sedimentary rocks and diagenetic features constitutes the main mission of ChemCam, a number of discoveries have also been made about igneous rocks and about Martian soil in general. The results of some of these unique ChemCam findings are described briefly below. The Discussion section returns to the major goal of ChemCam during Curiosity's exploration, which is to provide broad coverage of the sedimentary strata in Gale and to aid our understanding of its fluvial history.

RESULTS

First Window into the Components and Hydration of Martian Soil

On sol (Mars day) 13 of the landed mission, the first ChemCam observation was made on a small float (i.e. not outcropping) rock in front of the rover. The spectrum from the first laser shot showed a substantial hydrogen emission peak. This peak disappeared in subsequent shots, which would have been dust-free. The immediate implication

was that Martian dust is hydrated, which was confirmed by the first laser shot on each rock target analyzed and by all laser shots on soil targets. The quantification of H by ChemCam is still in progress. The hydration of Martian soil and dust was also detected by the dynamic albedo of neutrons (DAN) and sample analysis at Mars (SAM) instruments: 1.5–3 wt% H₂O was reported in the first soil that was sampled by SAM (Leshin et al. 2013). ChemCam observations throughout the mission have shown that soil hydration is ubiquitous, which is consistent with orbital observations that show a ubiquitous 3 μm absorption associated with H₂O absorbed onto minerals and the presence of hydrated phases (e.g. Milliken et al. 2007).

ChemCam soil observations have provided the first window into the compositional makeup of individual soil grains. During each soil observation, the laser beam digs a pit several millimeters deep (e.g. inset in FIG. 2A), typically using 30 shots fired within 10 seconds. Fine grains are removed immediately, whereas several laser shots are usually required to remove coarser soil grains. Time-lapse images have shown the progression

of these soil observations, and shot-to-shot variations in the spectral peaks and the total optical emission clearly distinguish between the fine and coarse soil grains (Cousin et al. 2014). Chemical results show that coarse grains have a significantly different composition from the fine grains (Meslin et al. 2013). The coarser grains are not strongly hydrated and for the most part correspond to the composition of local rocks, showing for the first time a local soil component, which is contrary to the idea that Martian soil is uniform across the planet. Probing of the finer grains showed that these are predominantly lower in SiO₂ (37–43 wt%) than average Martian soil (45.4 wt%; Taylor and McLennan 2009) and are clearly hydrated (FIG. 2c, INSET). The fine-grained component observed by ChemCam corresponds quite closely to the composition inferred for X-ray-amorphous soil constituents; this composition is obtained by subtracting the composition of the minerals observed by the CheMin instrument from the bulk soil composition determined by the APXS (Blake et al. 2013). Iron is an exception; it is depleted by a factor of almost two in the ChemCam observations of fine grains (Meslin et al. 2013) relative to the APXS results. Given the very different ways that ChemCam and the APXS observe these samples, it is possible that this difference is due to weathering-related iron depletions on the surfaces of these grains.

Coarse-Grained Feldspar-Rich Rocks

Imaging Observations

A number of igneous float rocks have been observed, with a variety of grain sizes. These rocks are considered igneous because of their clearly defined coarse mineral grains; some of these mineral grains correspond very well in appearance to feldspar and pyroxene grains. There is a strong correspondence between the visual and compositional identities of these grains. They also lack the hydrogen signature seen in fine-grained (presumably sedimentary) rocks and soils at Gale Crater (Schroeder et al. 2014). As more observations were made, it became clear that feldspar compositions occurred not only in float rocks but also in a majority of the clasts in some conglomerates (Williams et al. 2013). Coarse-grained, feldspar-rich float rocks were seen at Bradbury Rise in the early part of the mission (Sautter et al. 2014) and again a year later while the rover was traversing back past the landing site towards Mount Sharp. The insets in FIGURE 4 show two feldspar-rich clasts, Bindi and Horlick. Bindi, in particular, is one of a number of clasts that show a

high concentration of light-toned, elongated crystals more than 1 cm in length.

In contrast to the float rocks shown in FIGURE 4, the rock called Jake Matijevic (or Jake_M) (Stolper et al. 2013)—the first rock analyzed jointly by the APXS and ChemCam—did not present optically observable mineral grains despite examination at close range by the Mars hand lens instrument (MAHLI). Both the APXS and ChemCam chemical observations revealed significant compositional heterogeneity. The ChemCam observations did not correspond to known igneous mineral compositions, with the exception of one pyroxene grain (Stolper et al. 2013). Jake_M appears similar to a class of rocks observed capping local topographic highs; however, there is doubt about the igneous origin of these rocks due to an apparent lack of an igneous source, the lack of an igneous grain texture on the rock surface, and the appearance of rounded pebbles on its more weathered surface. The presence of pebbles is obvious in more recently observed rocks of similar composition and texture.

Spectral Observations

The main panel of FIGURE 4 shows molar Al/Si versus molar (Fe + Mg)/Si for observation points on the clasts Bindi and Horlick, determined using calibrated peak areas (univariate analyses; Wiens et al. 2013; Fabre et al. 2014). Overall, the Bindi spectra (not shown here) indicate strong enrichments of Si, Al, Na, K, Ca, and Rb and very weak to nonexistent Fe, Mg, and Ti peaks (cf FIG. 2). The calibrated spectra yield compositions that are consistent with nearly pure alkali feldspar for three of the observation points and with a high fraction of alkali feldspar for the other two points. The observation points corresponding to the nearly pure feldspars are within the very light-toned mineral grains, while the other two points are near or overlapping the edges of the feldspar grains (FIG. 4, INSET). In contrast, the spectra of another igneous clast, Horlick, which has finer grains, show less Si, Ca, Al, Na, and K, as well as more significant fractions of Fe and Mg, and some Ti. None of the Horlick data points lie directly on the y-axis in FIGURE 4, which is consistent with the smaller grain sizes in that target and the lower probability of placing the beam entirely on a single mineral grain. The Horlick data points define a trend that lies within the range of the Bindi points and extends from the alkali feldspars toward a clinopyroxene composition at a position of 0.5 on the x-axis.

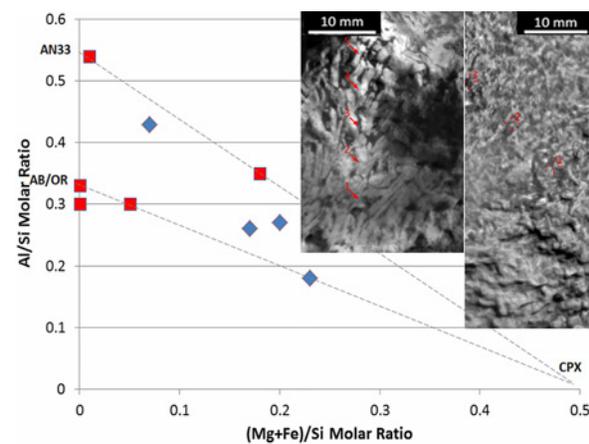


FIGURE 4 Compositions of feldspar-rich igneous clasts, Bindi and Horlick, obtained by ChemCam and, inset, ChemCam RMI images of the clasts. The red marks on the images indicate LIBS observation points. The compositions of these points are plotted as molar Al/Si vs molar (Fe + Mg)/Si. The y-axis and the x-axis represent felsic and mafic compositions, respectively. Mixing trends between clinopyroxene (CPX) and either pure albite/orthoclase (AB/OR) or AN₃₃ (33 mole percent anorthite) are indicated by light-colored dashed lines. IMAGES COURTESY OF NASA/JPL-CALTECH

Alkaline basalts were previously encountered by MER-A (Spirit rover) in the Columbia Hills in Gusev Crater. Examples of these were Backstay, Irvine, and Wishstone (e.g. McSween et al. 2006), all of which are olivine normative. In stark contrast to the inferred mineralogy from MER and that observed in a significant fraction of SNC meteorites, ChemCam has not observed individual olivine grains. Additionally, the compositions of some of the igneous float rocks in Gale are consistent with the presence of quartz and/or silica-rich glass. The overall conclusion from igneous rocks encountered along the traverse is that most are very different from those observed by MER, indicating more evolved magmas than previously encountered in surface observations on Mars. Indeed, fluorine, shown in the spectra in FIGURE 2, is present in these igneous rocks and in igneous clasts in conglomerates (Forni et al. 2014). Its occurrence, apparently in the form of fluorapatite, muscovite, and biotite, is also strongly suggestive of highly evolved magmas (Forni et al. 2014).

A second major difference from basalts previously encountered on Mars is the grain size and mineral occurrence. A number of the observed float rocks have centimeter-sized feldspar crystals, which are much larger than anything observed by MER or Pathfinder. The texture of Bindi (FIG. 4, INSET), in particular, is characteristic of a feldspar cumulate, never before seen on Mars, in which the density of feldspar causes it to segregate from the bulk of the magmatic material during crystallization.

Diagenetic Features and Alteration

Gale Crater is a sedimentary site, and the material along Curiosity's traverse in the crater consists overwhelmingly of sedimentary sandstones and mudstones. Most of ChemCam's observations have been dedicated to characterizing these materials to support our understanding of the fluvial activity that formed this site and of the setting's potential habitability. The small size of ChemCam's beam provides a unique capability to analyze fine-scale features within this sedimentary setting, including fine layering (FIG. 5A) and numerous diagenetic features (FIG. 5B-E). Curiosity's first destination in pursuing its goal of determining the stratigraphy of Gale Crater's sediments was the exposed Yellowknife Bay formation, located to the east of Bradbury Landing and several meters lower in elevation (Grotzinger et al. 2014). Upon entering the lower member, called Sheepbed (FIG. 3), images from Navcam and Mastcam indicated the presence of light-toned veins. ChemCam analyzed the first of these at a rock target named Crest and identified the light-toned material as calcium sulfate (FIG. 5E). Among the many other Ca sulfate veins and nodules, several levels of hydration were observed (Nachon et al. 2014), suggesting gypsum or bassanite—the two forms of hydrated calcium sulfate—or both. A majority of these Ca sulfate observations were in the stratigraphically lowest member (Sheepbed), which consists of mudstones, though some observations extended into the overlying coarser sandstones (referred to as the Gillespie Lake member; see FIG. 3). Recently, calcium sulfates have been observed more regularly along the traverse. They highlight an episode of relatively mild, low-temperature (<50°C) fluid circulation inside cracks formed after the cementation of the sediments during an earlier diagenetic period.

Gale Crater displays manifold evidence of eolian erosion: many of the rocks display exotic forms—fins, flutes, facets, and grooves—due to the carving action of the wind. It was therefore surprising to find surface alteration in one particular target using ChemCam's depth profiling capability. Ollila et al. (2014) found that early shots at three of the five observation points at Bathurst Inlet (sol 55) indicated enrichments of mobile elements at the surface by factors of ~2 relative to the last few shots (shots 26–30) at each

location. The greatest enrichment was in Li, followed by Rb, and then by Na and K. The enrichments suggest either leaching or a deposition of mobile elements on the surface. Given the eolian erosion of most rocks, this result seems to indicate relatively recent aqueous transport of mobile elements in at least a few places in Gale Crater.

A number of locations have revealed high concentrations of manganese. The occurrence of oxidized Mn-rich minerals (indicated by abundances well above 1 wt% MnO) requires a strongly oxidizing fluid. High Mn abundances were sporadically observed in the first 1.5 years of the mission, and these observations were not generally correlated with any surface features that might help explain the production of Mn-rich minerals. One example is the target Caribou on sol 342 (Fig. 5D; Lanza et al. 2014), where only one point in a line scan of LIBS observations indicated high Mn. A dark albedo around this point may suggest a Mn-rich coating, but there are no other clues. Manganese-rich surface material was also discovered by ChemCam observations on targets Stephen and Neil (sol ~615). In this case the rock surface was flat, dark, and shiny (Fig. 1), and the manganese was uniformly distributed across the surface. Numerous ChemCam depth profiles indicated that the layer is relatively thin, and other trace elements were shown by APXS to correlate with Mn, all suggesting that this material was a fluid-deposited fracture fill. The production pathway for manganese-rich minerals on Mars is at this point unclear. Although Mars is considered somewhat oxidizing, as hematite occurs in abundance, the oxygen content of the current atmosphere is low and would be insufficient to produce manganese-rich minerals, as was also the case with the early Earth prior to the great oxygenation event.

DISCUSSION AND CONCLUSIONS

Chemostratigraphy

Gale Crater represents a new type of site for in situ exploration on Mars. Although Spirit rover also landed in a large crater with an inflow channel, the goal of finding a fluvial location on Mars was largely unrealized due to apparent lava infilling Gusev Crater. In the case of Gale Crater, although a larger flow channel exists at the southern edge of the crater, the Peace Vallis channel and associated alluvial fan can be traced directly into the landing ellipse from orbital images (Fig. 3). Thus, the prelanding data suggested a much greater likelihood of encountering fluvially transported materials in Gale. The mission has not disappointed in this respect, and it is clear that a very large volume of fluvially transported material has infilled the portion of Gale Crater traversed by Curiosity.

Given these findings, several key questions involve, first, placing constraints on the source materials based on compositions and, second, understanding the alteration history of the sediments. *Chemostratigraphy*, the study of chemical variations among sediments, has been used extensively in studying the Precambrian terrestrial record. These studies have taken many different forms, including various isotope ratio measurements that can be made easily (e.g. carbon, oxygen, strontium) and element ratios and abundances, such as iron-speciation data, the chemical index of alteration, and rare earth element profiles. ChemCam provides the ability to perform numerous analyses in a short time at an outcrop or stratigraphic section, facilitating chemostratigraphy in terms of major elements, hydration level, and key trace elements. This capability has been put to use in several different locations where the rover stopped. The first such location was at Rocknest (sol 56), a cluster of boulders that trapped eolian drifts, where Curiosity stopped to perform its first soil analyses. While there, ChemCam performed multiple analyses on a suite of iron-rich rocks of widely differing textures and found that there was no correlation between rock compositions and textures (Blaney et al. 2014). A second general area included the lower members of the Yellowknife Bay formation, namely Sheepbed and Gillespie Lake, and the Point Lake unit of the Glenelg member (Fig. 3). The correlated combination of textural and compositional observations made by ChemCam provided strong evidence for interpreting the relationships between these members. For example, the composition of the Gillespie Lake member, a sandstone, was found to be similar to the underlying Sheepbed member. Sheepbed is a finer-grained mudstone, which was shown by CheMin to contain phyllosilicates (Vaniman et al. 2014). Although no CheMin analyses were carried out on the Gillespie Lake member, ChemCam analyses indicated that it too is hydrated, implying that phyllosilicates are present as a cementing agent in this sandstone as well as in the mudstone. These results support our understanding of alteration and hence of the depositional environment of these strata.

A third location studied during the first year of the mission was Shaler, a thinly layered outcrop ~20 m long and a little more than 1–1.5 m thick; in this outcrop, alternating erosion-resistant and recessive strata were exposed (e.g. Anderson et al. 2014). The outcrop was too rugged to consider driving over it to place the arm on the seven different identified facies. Despite this limitation, the rover team was able to rapidly sample the facies from a distance, analyzing 26 different targets. The results showed broadly similar compositions across the different facies for most of the major elements, but revealed a distinct enrichment of potassium in the uppermost part of the outcrop, suggesting variable inputs of orthoclase-rich material from somewhere

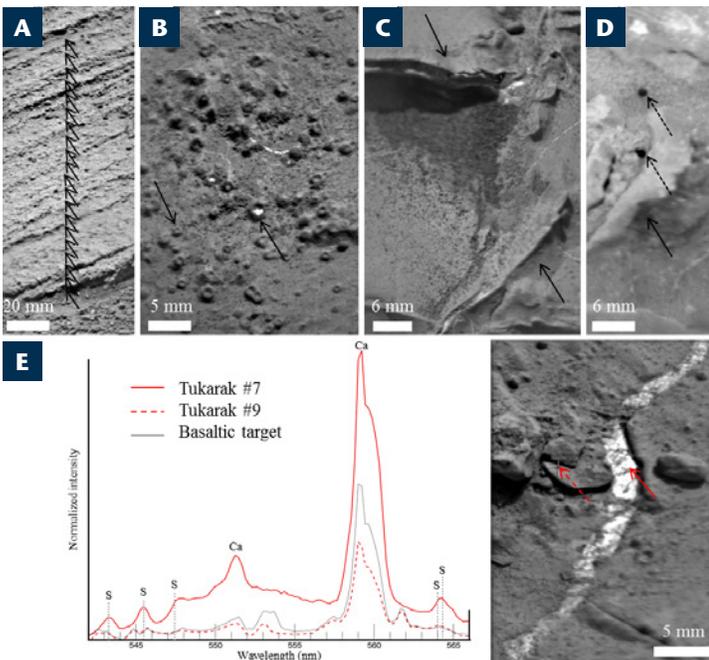


FIGURE 5 Fine-scale features observed by ChemCam, including (A) a transect of a target from Facies 4 of the Shaler outcrop and (B–E) diagenetic features, indicated by arrows, observed by ChemCam’s RMI. (A) Wakham Bay target with locations of LIBS points (sol 311). (B) Nodules in target Rae (sol 192). (C) Raised Mg-rich ridges in Rowatt (sol 133). (D) Caribou (sol 342); the black arrow indicates an observation point yielding a high (>50 wt%) MnO concentration. Two laser pits in soil can be seen above this point (dashed arrows). Panel (E) shows a calcium sulfate vein in Tukarak (sol 157); the red full arrow indicates the location of the ChemCam analysis displaying a calcium sulfate signature, as shown in the accompanying spectrum; the dashed arrow corresponds to the dashed spectrum without S and Ca enrichment. The spectrum of a typical basaltic target is shown for comparison. IMAGES COURTESY OF NASA/JPL-CALTECH

upstream. Subsequently, the rover team has found even greater potassium enrichments at a more recent site named Kimberley (Fig. 3).

An important observation from Gale Crater sediments is that while the conglomerates contain clasts reflecting the compositions of the igneous float rocks (e.g. Williams et al. 2013), finer-grained sediments, including all the units at Yellowknife Bay (Grotzinger et al. 2014), are much closer in composition to Martian soil and dust (McLennan et al. 2014). CheMin results showed that >30% of the Sheepbed mudstone in Yellowknife Bay consists of alteration products, including ~20% as smectite clays (Vaniman et al. 2014). The simplest explanation is that the fine-grained material was carried from a more distant source than the larger conglomerate clasts. Although the source of the fine-grained material might be farther into the source region of Peace Vallis, there is no way to confirm this idea at present, and other source regions are possible, given that Gale Crater has many inflow channels.

Future Prospects

As of early 2015, Curiosity has traveled more than 9 km in the direction of Mt. Sharp and is now in rough terrain well outside of its landing ellipse (Fig. 3). As the rover gains elevation onto the lower flanks of the mountain, spectral features seen from orbit (e.g. Anderson and Bell

2010) are expected to be observed by the rover instruments. These include increased phyllosilicates and hematite, the latter of which has been observed from orbit along a ridge ("Hematite Ridge" in Fig. 3). Indeed, around sol 725 ChemCam's passive spectra began showing features indicative of iron oxides and sulfates. Additionally, exploration of the Pahrump Hills outcrop (Curiosity's current location; sols 750 to >870) shows compositions indicative of increased alteration, consistent with the phyllosilicates observed from orbit. Exploration of the regions ahead will hopefully elucidate the origins of these features and provide clues to the formation of Mt. Sharp, and possibly of the regional Medusa Fossae formation.

ACKNOWLEDGMENTS

This work was supported by the NASA Mars Program Office in the US and by the French Space Agency (CNES) in France. Ryan Anderson, Fred Calef, Zareh Gorjian, Stéphane Le Mouélic, Nicolas Mangold, Marion Nachon, William Rapin, Sam Clegg, Cécile Fabre, Agnes Cousin, and Violaine Sautter are thanked for their contributions to this work. The Jet Propulsion Laboratory is thanked for and congratulated on its excellent development and support of the MSL mission. The manuscript benefited from constructive reviews by R. Arvidson and G. Rossman, and from editorial support by J. Grotzinger and G. Brown. ■

REFERENCES

- Anderson RB, Bell JM III (2010) Geologic mapping and characterization of Gale crater and implications for its potential as a Mars Science Laboratory landing site. *Mars 5*: 76-128
- Anderson RB and 28 coauthors (2014) ChemCam results from the Shaler outcrop in Gale Crater, Mars. *Icarus*, doi: 10.1016/j.icarus.2014.07.025
- Blake DF and 45 coauthors (2013) Curiosity at Gale Crater, Mars: characterization and analysis of the Rocknest sand shadow. *Science* 341, doi: 10.1126/science.1239505
- Blaney D and 27 coauthors (2014) Chemistry and texture of the rocks at "Rocknest", Gale Crater: evidence for iron-rich cements. *Journal of Geophysical Research Planets* 119: 2109-2131
- Cousin A and 28 coauthors (2014) Compositions of coarse and fine particles in Martian soils at Gale: a window into the production of soils. *Icarus*, doi: 10.1016/j.icarus.2014.04.052
- Cremers DA, Radziemski LJ (2006) *Handbook of Laser-Induced Breakdown Spectroscopy*. Wiley, 283 pp. Available online at <http://onlinelibrary.wiley.com/book/10.1002/0470093013>
- Fabre C and 11 coauthors (2014) In situ calibration using univariate analyses based on the onboard ChemCam targets: first prediction of Martian rock and soil compositions. *Spectrochimica Acta Part B: Atomic Spectroscopy* 99: 34-51
- Forni O and 13 coauthors (2014) First fluorine-bearing mineral detections on Mars, with ChemCam on MSL. 45th Lunar and Planetary Science Conference, Abstract # 1328
- Grotzinger JP and 72 coauthors (2014) A habitable fluvio-lacustrine environment at Yellowknife Bay, Gale crater, Mars. *Science* 343, doi: 10.1126/science.1242777
- Lanza NL and 20 coauthors (2014) High manganese concentrations in rocks at Gale Crater, Mars. *Geophysical Research Letters* 41: 5755-5763
- Leshin LA and 34 coauthors (2013) Volatile, isotope, and organic analysis of Martian fines with the Mars Curiosity rover. *Science* 341, doi: 10.1126/science.1238937
- Maurice S and 69 coauthors (2012) The ChemCam instrument suite on the Mars Science Laboratory (MSL) rover: science objectives and Mast Unit description. *Space Science Reviews* 170: 95-166
- McLennan SM and 50 coauthors (2014) Elemental geochemistry of sedimentary rocks at Yellowknife Bay, Gale crater, Mars. *Science* 343, doi: 10.1126/science.1244734
- McSween HY and 13 coauthors (2006) Alkaline volcanic rocks from the Columbia Hills, Gusev Crater, Mars. *Journal of Geophysical Research Planets* 111: E09S91, doi: 10.1029/2006JE002698
- Meslin P-Y and 60 coauthors (2013) Soil diversity and hydration as observed by ChemCam at Gale Crater, Mars. *Science* 341, doi: 10.1126/science.1238670
- Milliken RE and 6 coauthors (2007) Hydration state of the Martian surface as seen by Mars Express OMEGA II: H₂O content of the surface. *Journal of Geophysical Research Planets* 112: E08S07, doi: 10.1029/2006JE002853
- Nachon M and 33 coauthors (2014) Calcium sulfate veins characterized by the ChemCam instrument at Gale Crater, Mars. *Journal of Geophysical Research Planets* 119: 1991-2016
- Ollila AM and 32 coauthors (2014) Trace element geochemistry (Li, Ba, Sr, and Rb) using Curiosity's ChemCam: early results for Gale Crater from Bradbury Landing Site to Rocknest. *Journal of Geophysical Research Planets* 119: 255-285
- Pike WT and 7 coauthors (2011) Quantification of the dry history of the martian soil inferred from in situ microscopy. *Geophysical Research Letters* 38: L24201, doi: 10.1029/2011GL049896
- Sautter V and 22 coauthors (2014) Igneous mineralogy at Bradbury Rise: the first ChemCam campaign at Gale Crater. *Journal of Geophysical Research Planets* 119: 30-46
- Schroeder S and 15 coauthors (2014) First analysis of the hydrogen signal in ChemCam LIBS spectra. *Icarus*, doi: 10.1016/j.icarus.2014.08.029
- Squyres SW and 11 coauthors (2003) Athena Mars rover science investigation. *Journal of Geophysical Research Planets* 108: 8062, doi: 10.1029/2003JE002121
- Stolper EM and 18 coauthors (2013) The petrochemistry of Jake_M: a martian mugearite. *Science* 341, doi: 10.1126/science.1239463
- Taylor SR, McLennan SM (2009) *Planetary Crusts: Their Composition, Origin, and Evolution*, Cambridge University Press, Cambridge, 404 pp
- Vaniman DT and 35 coauthors (2014) Mineralogy of a mudstone at Yellowknife Bay, Gale crater, Mars. *Science* 343, doi: 10.1126/science.1243480
- Wiens RC and 79 coauthors (2012) The ChemCam instrument suite on the Mars Science Laboratory (MSL) rover: body unit and combined system tests. *Space Science Reviews* 170: 167-227
- Wiens RC and 22 coauthors (2013) Pre-flight calibration and initial data processing for the ChemCam laser-induced breakdown spectroscopy instrument on the Mars Science Laboratory rover. *Spectrochimica Acta Part B: Atomic Spectroscopy* 82: 1-27
- Williams RME and 37 coauthors (2013) Martian fluvial conglomerates at Gale Crater. *Science* 340: 1068-1072 ■