

# Geochemical profile of a layered outcrop in the Atacama analogue using laser-induced breakdown spectroscopy: Implications for Curiosity investigations in Gale

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[1] We performed laboratory laser-induced breakdown spectroscopy (LIBS) and laser Raman spectroscopy measurements on samples from a layered outcrop from the Atacama Desert, Chile. This outcrop is a terrestrial morphological and possibly mineralogical analogue for similar formations that will likely be investigated by the Curiosity rover at Gale Crater. Our results demonstrate that fast LIBS analysis can generate semiquantitative chemical profiles in subminute times using automated data processing tools. Therefore, the LIBS instrument can be an invaluable tactical tool on the Curiosity rover for remote, rapid geochemical survey of layered outcrops, thus serving daily operational needs. The derived chemical profiles, supported by the range of minerals identified by Raman spectroscopy, is consistent with the products of a continental evaporitic lake. In the framework of future surface exploration on Mars, a combined Raman/LIBS investigation may provide a rapid mineralogical/chemical evaluation of targets that can be useful for selecting samples to be eventually collected for sample return purposes or for selecting sample sites to be drilled in the search for astrobiology-relevant species. **Citation:** Sobron, P., C. Lefebvre, R. Leveille, A. Koujelev, T. Haltigin, H. Du, A. Wang, N. Cabrol, K. Zacny, J. Craft, and The LiTA 2012 Team (2013), Geochemical profile of a layered outcrop in the Atacama analogue using laser-induced breakdown spectroscopy: Implications for Curiosity investigations in Gale, *Geophys. Res. Lett.*, 40, 1965–1970, doi:10.1002/grl.50261.

## 1. Introduction

[2] The chemistry and the stratigraphy of sedimentary deposits are indicators of their depositional environment

and climate, and the evolution of these over time. Over the past eight years, the Mars Exploration rovers have investigated several outcrops at Meridiani Planum and Gusev Crater [Grotzinger *et al.*, 2005, 2006; Metz *et al.*, 2009; Ming *et al.*, 2008; Morris *et al.*, 2008, 2010; Squyres *et al.*, 2004]. These investigations have provided a deep understanding of the role of aqueous environments and atmospheric activity in the local sedimentary history.

[3] Compared to the Mars Exploration rovers, the capabilities of the Mars Science Laboratory (MSL) rover, Curiosity, to investigate outcrops and other deposits are enhanced by means of its sophisticated science instruments; one of them is a stand-off laser-induced breakdown spectroscopy (LIBS) instrument within the ChemCam suite [Wiens *et al.*, 2012]. ChemCam's LIBS instrument has the capability to obtain chemical information from a large variety of targets at various distances, up to 7 m, including distant targets within stratigraphic layers inaccessible by arm-deployed payload elements. Owing to its submillimeter laser spot size, it is expected that ChemCam will be able to map out the chemical stratigraphy of fine layers using quantitative analysis methods.

[4] With this work, we demonstrate, for the first time, that semiquantitative chemical stratigraphy can be very rapidly obtained by performing LIBS measurements on visually distinct layers within an outcrop at a terrestrial Mars analogue located in the Atacama Desert of Chile. Such semiquantitative chemical stratigraphy provides critical information on the distribution of elements across the layers, which can be used for tactical mission operation purposes.

## 2. Mars Analogue Setting and Analytical Methods

### 2.1. Layered Outcrop at the Atacama Desert, Chile

[5] Figure 1 shows the layered outcrop in the Valle de los Dinosaurios (VD), Atacama, Chile, that we investigated. Our investigation was performed within the context of the Subsurface Life in the Atacama (LiTA) project, supported by the NASA Astrobiology Science and Technology for Exploring Planets program [Cabrol *et al.*, 2013]. The outcrop we investigated during the first field campaign of the LiTA project is located at 22.910278°S and 68.235833°W at 2621 m above sea level within the Cordillera de la Sal formation. Previous stratigraphic work in the Cordillera de la Sal revealed the presence of gypsum, anhydrite, and halite, interpreted as having been deposited in an alluvial-fan to playa-lake environment [Dingman, 1967; Flint, 1985]. The outcrop in Figure 1 represents a ~2 m

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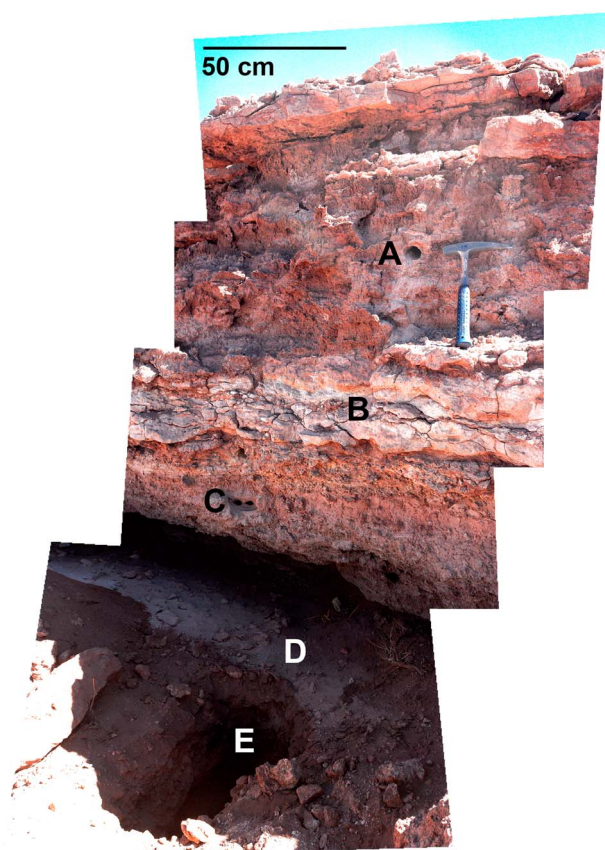
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**Figure 1.** Image of the layered outcrop at Valle de los Dinosaurios, Atacama, Chile. The material diversity in the outcrop identified in the field includes: pancake and caliche with inclusion of angular pebbles to blocks, volcanic pebbles (angular to subangular), and volcanic and sedimentary granules. The underlying material is composed of a layer of fine volcanic sand. Labels indicate the approximate location of the sample drilling and collection. Samples were collected at each of the layers labeled A to E.

thick exposure that appears to be composed of a consolidated mix of clay, sulfates, and halides.

[6] Near-vertical outcrops comprising individual layers of submeter thickness are also present at numerous locations within the MSL landing ellipse, including one less than 1.5 km from the location where Curiosity touched down on 5 August 2012, as depicted in Figure S1 in the auxiliary material. Remote orbital investigations of the MSL landing ellipse previously revealed the presence of an unidentified light-toned, high thermal inertia unit, which has been interpreted as a cemented sedimentary unit [Anderson and Bell, 2010; Golombek et al., 2012]. While visible and near-infrared (VNIR) spectral analyses do not provide definitive mineralogical compositions for this unit, several locations near the base of Mount Sharp, the prime target of the MSL mission, clearly show various Ca- and Mg-sulfates and Fe- and Mg-clay minerals as observed by the CRISM instrument on the Mars Reconnaissance Orbiter [Milliken et al., 2010]. Carbonate minerals have yet to be clearly identified in Gale Crater, although they are known to occur at several locations on the surface, within Martian dust, and within some Martian meteorites [Bandfield et al., 2003; Boynton et al., 2009; Ehlmann et al., 2008b; McKay

et al., 1996; Morris et al., 2010]. The presence of halides on Mars has also been inferred from studies of meteorites and recent orbital spectra [Glotch et al., 2010; Osterloo et al., 2008]. Even if there are geochemical and mineralogical differences between our study site in the Atacama and similar exposures on Mars, the obvious structural similarities make the VD outcrop an appropriate morphological analogue, and provide a possible case-study for improving Curiosity's tactical operations.

[7] We collected five samples from the five distinct layers in the VD outcrop shown in Figure 1. The samples were collected as powdered rocks and soil using a purpose-built auger-type drilling instrument developed by Honeybee Robotics [Zacny et al., 2012] that will be deployed by the LiTA's rover in upcoming rover field campaigns. This drilling instrument was used to sample each of the layers labeled in Figure 1, horizontally, to a depth of ~20 cm. Sample drilled within the first centimeter was discarded because it contained dust and likely weathered material. The obtained powdered samples were packed and sealed in plastic bags, and later pressed into pellets prior to LIBS analysis.

## 2.2. Instrumentation

[8] Our LIBS setup, described elsewhere [Koujelev et al., 2010], included a laser, optical elements to focus the laser beam and to collect plasma emission, and a spectrometer. For each sample, 100 spectra were collected from 10 different spots. We used five cleaning shots per spot to remove any surface contamination. Raman spectra were collected with the same Raman instrumentation we used in previous work [Kong et al., 2011]. For each sample, five spectra were collected from five random spots.

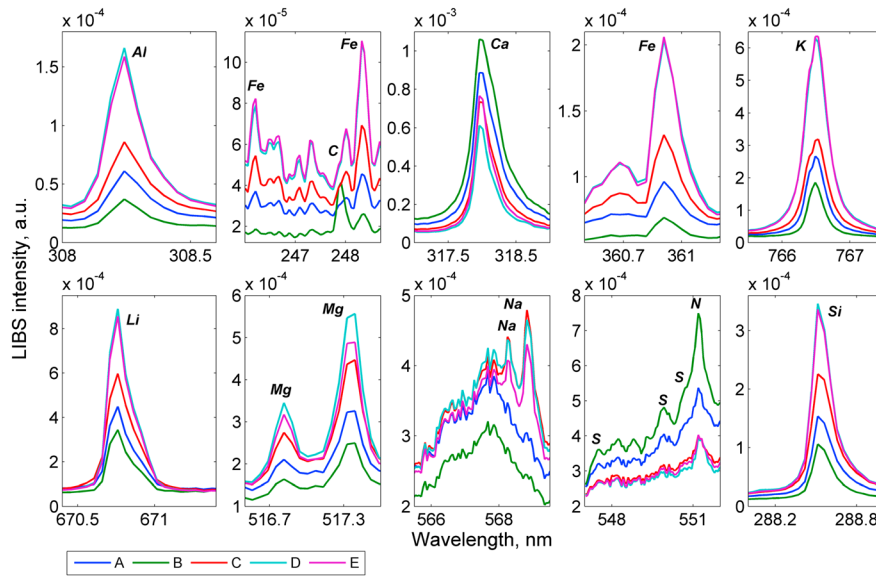
## 3. Results

### 3.1. Chemistry Through LIBS Data Analysis

[9] The LIBS spectra of the five samples were preprocessed following the procedure described by [Sobron et al. 2012]. The conditioning routines include subtraction of continuum background, normalization to the total emission integrated intensity area of each spectrum, and spectra averaging. The spectral normalization also allows sample-to-sample comparison of the results from the analysis described below. The LIBS spectra of the five samples are shown in Figure 2.

[10] To identify specific elements within the samples, the preprocessed LIBS spectra were compared to a spectral database that includes lines from the National Institute of Standards and Technology Atomic Database [Kelleher et al., 1999; Ralchenko et al., 2010], lines from the recently published Mars emission line library [Cousin et al., 2011], and lines from our own spectral libraries [Koujelev et al., 2010; Lui and Koujelev, 2011; Sobron et al., 2012]. Here, we constrained the database search to Al, C, Ca, Fe, K, Li, Mg, Na, S, and Si, as they are typical of most rocks and soils relevant to our investigation. The wavelengths and the type of the emission lines used for identification are listed in Table 1.

[11] Because the goal of this work is to demonstrate the capabilities of LIBS for rapid geochemical investigation for tactical mission operations, we used a semiquantitative approach for deriving layer-to-layer variations in elements concentrations within the VD outcrop. Given the proportional



**Figure 2.** LIBS spectra of layers A to E in selected regions of interest. The spectra were normalized to the total emission area.

**Table 1.** Spectral Lines of the Elements Used in This Work Displayed in Wavelength Order. Transition Type in Brackets

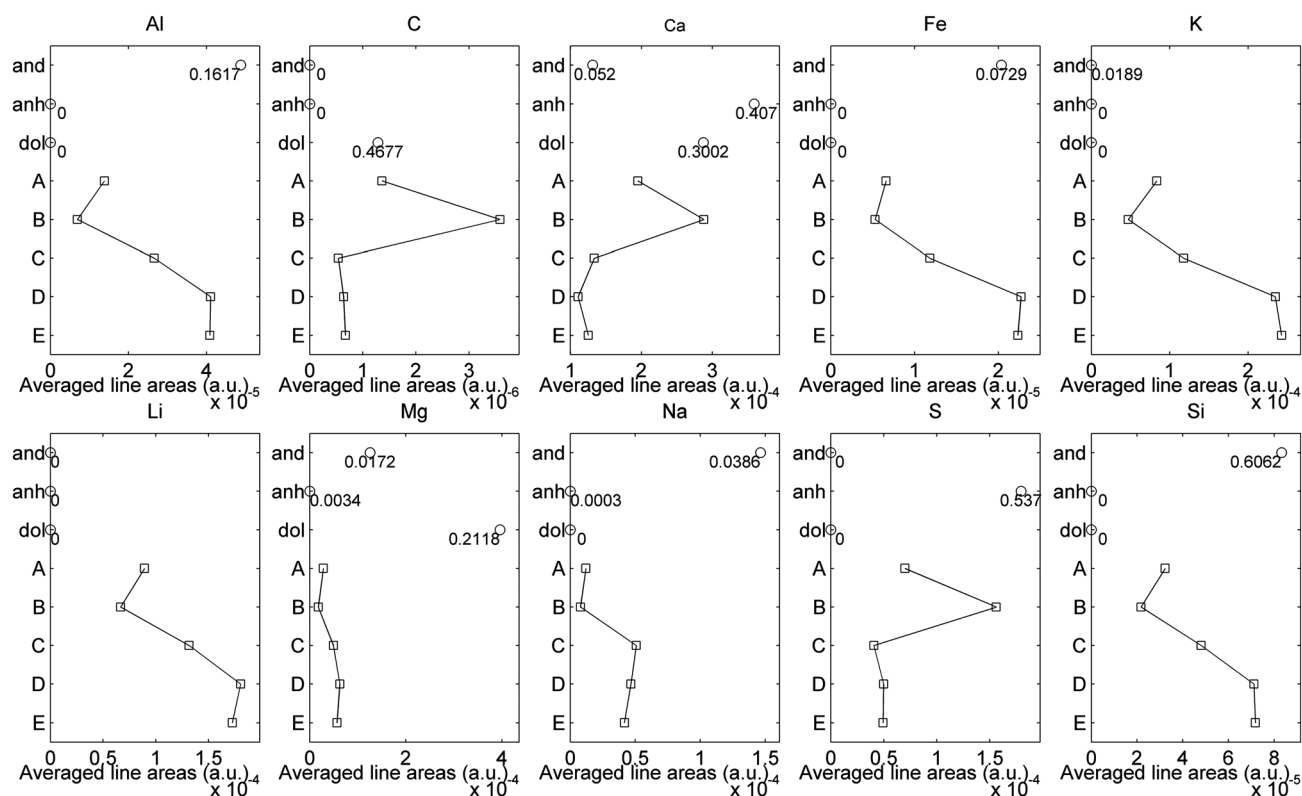
Element Emission Line (nm)								
Al	(I) 308.2	(I) 309.3						
C	(I) 247.8							
Ca	(II) 315.9	(II) 317.9	(II) 370.6	(II) 373.7	(I) 643.9	(I) 645.0	(I) 645.5	(I) 646.2
Fe	(I) 356.5	(I) 361.9	(I) 438.4	(I) 440.5				
K	(I) 766.5	(I) 769.9						
Li	(I) 670.8							
Mg	(I) 516.8	(I) 517.3						
Na	(I) 330.2	(I) 568.2	(I) 568.8					
S	(II) 547.5	(I) 549.8	(II) 550.7					
Si	(II) 288.6							

relationship between the area of the emission lines of an element in a LIBS spectrum and the concentration of this element in a sample [Cremers and Radziemski, 2006; Miziolek et al., 2006; Noll, 2012], our approach is based in computing the relative areas of the 26 lines listed in Table 1. The specific lines were isolated from the complex spectral envelopes and their areas calculated using nonlinear line fitting methods based on a customized version of the Marquardt-Levenberg algorithm [Sobron et al., 2008]. The results are plotted in Figure 3. Three certified reference samples: andesite, anhydrite ( $\text{CaSO}_4$ ), and dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ], were also analyzed, and the results plotted for reference. Because the LIBS spectra of the outcrop samples and the certified reference samples were normalized to the emission integrated total area, the plots in Figure 3 allow evaluating layer-to-layer variations in the relative concentration of each element within the outcrop, thus providing a semiquantitative multielement chemical profile of the outcrop.

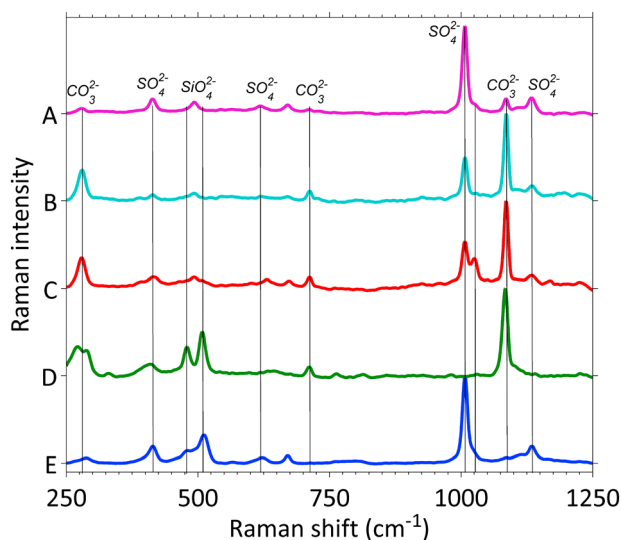
### 3.2. Mineralogy Through Raman Analysis

[12] Figure 4 displays the averaged Raman spectra for each of the five samples. The peaks at 1007 and 1133  $\text{cm}^{-1}$  observed in spectra of samples A, B, C, and E are

assigned to the  $\nu_1$  symmetric stretching vibrations and  $\nu_3$  asymmetric stretching vibrations of sulfate ions in gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) [Chio et al., 2004; Krishnamurthy and Soots, 1971; Sarma et al., 1998]. The relatively less intense set of peaks centered at  $\sim 400$  and  $625 \text{ cm}^{-1}$  are assigned to the  $\nu_2$  and  $\nu_4$  asymmetrical bending vibrations of sulfate also in gypsum. The Raman spectra of samples A and C, and E (strong peak in C, weak shoulder in A and E) show an additional peak at  $1026 \text{ cm}^{-1}$ , which matches approximately the position of the  $\nu_1$  sulfate vibrational mode in alunite [ $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ] reported by Frost et al. [2006], although the peaks  $< 700 \text{ cm}^{-1}$  do not match those of alunite; the identification of alunite is therefore not definitive. All of the samples show peaks at 1086, 711, and 280  $\text{cm}^{-1}$ , which can be attributed to the  $\nu_1$  and  $\nu_4$  vibrational and the  $L_1$  librational modes of calcite ( $\text{CaCO}_3$ ), respectively [Gunasekaran et al., 2006; Misra et al., 2005]. Calcite bands in sample E are very weak. The Raman spectra of sample D shows a doublet at 480/510  $\text{cm}^{-1}$ , typically associated to K-, Na-rich plagioclase [Mernagh, 1991]. The spectrum of sample E shows a complex envelope around 500  $\text{cm}^{-1}$ , which is consistent with a more vitrified phase of plagioclase [Fritz et al., 2011]. The envelope around 500  $\text{cm}^{-1}$  in samples D and E and other features



**Figure 3.** Chemical profiles of the layered outcrop (squares). The  $X$  axis represent the averaged derived line area of the emission lines associated to each element for each of the layers (squares) and for the three certified reference samples (circles): andesite (“and”), anhydrite (“anh”), and dolomite (“dol”). The abundance of elements for the three reference samples, in oxide percent, is shown next to the markers.



**Figure 4.** Raman spectra of layers A to E. The spectra are plotted in the 250–1250  $\text{cm}^{-1}$  region. The spectra have been normalized to the most intense peak in this range. The spectra are offset in the intensity axis, and annotated with the major species for clarity. The position and the intensity of the Raman peaks were used to identify the mineral phases present in the samples. Labels indicate the major groups identified.

across the entire spectral range can also be associated with certain clays [Wang and Sobron, 2011]. Because of the smaller Raman cross-section of silicates in general

relative to calcite and gypsum, the peaks associated to both the K-, Na-rich plagioclase and the vitrified plagioclase are very weak.

#### 4. Discussion

[13] The LIBS and laser Raman spectroscopy characterization of the outcrop at Valle de los Dinosaurios, Atacama, Chile, shows chemical and mineralogical variations across five layers. The semiquantitative chemical profile obtained through LIBS (Figure 3) suggests a relative enrichment in Al, Fe, K, Li, Mg, Na, and Si toward the middle to lower section of the outcrop (layers C, D, and E). C and Ca are relatively more abundant in the middle to upper sections of the outcrop (layers A, B, and C). Due to the poor sensitivity of LIBS to S in air and to the poor signal-to-noise ratio of the S lines in the visible spectral range, we can only conclude that S is present in layers A and B but not in the rest; or it is below detection limits. Our interpretation of these observations leads to a mineralogical profile in which there is a relatively higher abundance of Ca-rich sulfates and carbonates in the top two layers, and a higher abundance of multicationic silicates in the bottom layers. This interpretation is supported by the mineralogy data obtained through laser Raman spectroscopy of the collected samples; the major sulfates and carbonates have been identified as gypsum, possible alunite, and calcite. The identification of the silicates in samples D and E suggests the presence of K, Na-rich plagioclase and vitrified plagioclase.



These two phases are consistent with the Al, K, Na, Si enrichment in the bottom two layers of the outcrop detected by LIBS. The relative high abundance of Li in the C and D layers could be explained by the presence of Li-bearing clays, which typically results from the alteration of volcanic materials by alkaline brines in playa-like deposits. Note that the brines at the Salar de Atacama (located less than 20 km from the VD outcrop), are a major source of lithium [Melvin, 1991]. Due to the relative insensitivity of LIBS to Cl [Wiens *et al.*, 2011], and to the fact that ionic bonds are very weak Raman scatterers [Long, 1977], we have not identified halides such as halite (NaCl), which are typical in the evaporitic deposits in the VD region. Halides, while not identified, are likely to partially account for the presence of Mg and Na throughout the outcrop. Our interpretation of the geochemistry and mineralogy in the VD outcrop involves a continental evaporitic lake, where the evaporites are understood as being the products of deposition in a saline coastal lake, as documented by [Bell, 1991; Bell and Suarez, 1993]. The lower layers, likely richer in clastic silicate materials, may represent a higher energy environment, with perhaps some fluvial input.

[14] The VD outcrop may therefore be a reasonable morphological, geochemical, and environmental analog to similar outcrops in Gale Crater and elsewhere on Mars. The Curiosity rover landed near the toe of a putative alluvial fan coming off of the Western side of the Gale Crater rim and imagery suggests the presence of clastic and conglomerate-type rocks [Anderson and Bell, 2010]. In the first four months of the mission, the rover has traveled eastward toward a low-lying area known as Glenelg. It is very likely that this area has seen aqueous activity related to the distal parts of the alluvial fan, and possibly even playa-like accumulations of shallow water at the lowest elevations. Similar environments have also been inferred for parts of Meridiani Planum [Andrews-Hanna *et al.*, 2010].

[15] Based on results and our interpretation of the geological setting of the VD outcrop, it is likely that more than one layer would be promising for more detailed sampling and/or analysis by analytical instruments, either arm-mounted instruments or sampling systems, such as those on the Curiosity rover. Both sulfates and phyllosilicates represent priority targets for habitability studies because both types of minerals are likely recorders of aqueous processes and both may preserve organic molecules [Aubrey *et al.*, 2006; Ehlmann *et al.*, 2008a; Summons *et al.*, 2011]. In a realistic mission scenario, deciding on the specific layer to sample or to analyze in detail would benefit from additional imagery demonstrating sedimentary textures and grain sizes, and hypotheses on sedimentological facies models and provenance of the sedimentary layers. However, we have shown the benefit of rapidly acquiring LIBS elemental compositions to characterize individual layers of an outcrop to make tactical decisions during a planetary surface mission.

[16] Two main conclusions can be drawn from our results:

[17] (1) Semiquantitative LIBS data analysis can generate chemical profiles of layered outcrops. Furthermore, such chemical profiles can be obtained in subminute times using automated data processing tools running on an average-performance processor. For these two reasons, we believe that the LIBS instrument in the ChemCam suite can be used during MSL daily tactical operations for rapid geochemical survey of layered outcrops, and to support decision making

process, such as “to drive-away or to stay.” There exist morphologically, mineralogically, and environmentally analogous submeter layered outcrops to the VD outcrop in Gale crater. These will be important scientific targets during the MSL mission due to their high relevance to the mission’s primary objectives: to assess whether environments there were once habitable for microorganisms.

[18] (2) The information obtained from both LIBS and laser Raman spectroscopy facilitates detailed descriptions of the chemical profiles and the mineralogy of layered outcrops. From the perspective of a mission for planetary exploration, Raman/LIBS is a very attractive combination of chemical and mineralogical instruments that can rapidly provide detailed mineral phase identification with precise chemical characterization of all major, minor, and some trace mineral species. Such a combined investigation may provide a comprehensive mineralogical/chemical evaluation of the target that will be very useful for selecting samples to be eventually collected for sample return purposes, and for selecting sample sites to be drilled in the search for astrobiology-relevant species.

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