EVIDENCE FOR ROCK SURFACE ALTERATION WITH CHEMCAM FROM CURIOSITY'S FIRST 90 SOLS

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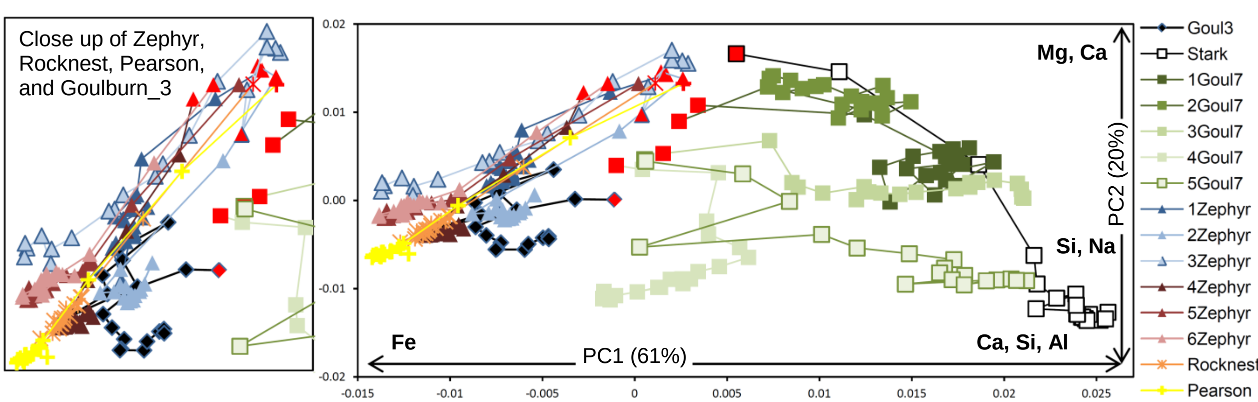
Introduction: On Earth, rock coatings and rinds may develop even in very arid environments through interactions between the rock surface, airborne dust, and moisture in the atmosphere. The composition and thickness of coatings and rinds provide much information about the style of chemical alteration (and amount of water) to which the rock has been exposed. As such, the potential observation of coatings or rinds on Mars provides information about both the climate and the presence and abundance of water in the surface environment. Previous studies have cited evidence for alteration on the surfaces of martian rocks [e.g. 1-3]. Here we discuss the current evidence for surface alteration as measured by the ChemCam instrument onboard the Mars Science Laboratory (MSL) rover mission 'Curiosity.'

Compositional depth profiles with ChemCam: ChemCam chemistry data are obtained using the laser induced breakdown spectroscopy (LIBS) instrument performing 30-50 laser shots in a single location, while context images are obtained with the Remote Micro Imager (RMI). Each individual shot returns a spectrum that represents the composition at a specific depth, with each subsequent shot sampling the composition at a slightly greater depth. Although the amount of material ablated by each shot varies by material, laboratory measurements of basalts have shown that each LIBS shot removes at least ~0.33-0.5 µm per shot [4], suggesting a removal of as much as ~25 µm of the surface for 50 shots. A sequence of individual shots in one location may be examined to understand changes in chemistry with depth. With a relatively small beam diameter (~400 microns at 3 m distance) and its sensitivity to many major and trace elements, ChemCam is able to detect subtle changes in chemistry with depth. As of the first 90 sols, neither the rock brush nor drill were deployed; as a result, all ChemCam data obtained thus far have been taken on unmodified natural rock surfaces.

Previous laboratory work: Previous studies [5, 6] have shown that LIBS can detect thin surface layers and distinguish them from the host rock beneath. In a study of naturally weathered terrestrial basalts, 50 shots were shown to penetrate rock varnish coatings averaging ~10 µm in thickness as well as part way into ~1 mm rinds beneath [5]. On Mars, coatings and rinds might be expected to be significantly thinner than terrestrial ones due to less available water, suggesting that ChemCam could be expected to be able to reach an unaltered rock composition well before 50 shots.

The signatures of coatings and rinds: What is expected? Depending on the style of alteration, there are several types of chemical trends that may be observed. Some common coatings, which may not be genetically related to the host rock, are regionally similar even when the underlying host rocks have different compositions. A common terrestrial example of this is rock varnish, which are found in arid regions and has essentially the same composition regardless of the compositions of the rocks on which it forms. In this case, LIBS-derived composi-

Fig. 1. Principal component analysis (PCA) scores plot of the selected sample set. Elements with the most influence are labeled along the PC1 and PC2 axes. The first 20 shots of each sample are represented, with a line connecting the shots in order of increasing number; all first shots are labeled in red. Data points that appear spatially close are more spectrally similar. Goulburn_7 and Stark show distinct compositions and compositional trends from all other samples.



tions of individual rocks would start out as very similar but become increasingly distinct from one another with depth. In contrast to coatings, rinds represent the addition, removal, or relocation of materials from the near-surface of the host rocks. Observation of a regional trend of cation depletion in rock surfaces would indicate the presence of weathering rinds formed by mobilization of particular cations during alteration. LIBS data would show rock compositions that are distinct from one another but an increase in particular cation abundance with depth would be observed.

Methods: *Data set:* A set of six rocks analyzed by ChemCam during the first 90 sols of the mission was selected: Goulburn_3 (single point), Goulburn_7 (1x5 raster), Stark (single point), Zephyr (3x3 raster, points 1-6 only), Rocknest_3 (depth profile), and Pearson (depth profile). This set includes multiple spots on Goulburn_7 and Zephyr for a total of 15 sampling locations. The first 20 shots of each sampling location were examined for a total of 300 individual LIBS analyses, which were normalized to the total emission to reduce the influence of laser fluctuations [e.g. 7]. These six rocks are located along the entire rover traverse and span a range of compositions [e.g. 8].

Rock surface evaluation: For each rock, RMI and MastCam images (when available) were evaluated for surface characteristics, including the presence of fine grained material visible near the LIBS shot location, apparent discoloration on the surface, and roughness.

Relative peak height evaluation: Each individual spectrum was examined for major and minor elements, including H; changes from shot to shot were noted in each sampling location. In addition, the first shots of each sampling location were compared.

PCA: In order to determine how similar each spectrum was to the others and what elements vary the most within the sample set, a number of principal component analysis (PCA) models were made using the commercially available software the Unscrambler. These models provide information about the chemical trends with depth.

Results: Rock surfaces have similar compositions in their first LIBS shots, after which the individual rock compositions become distinct from one another (e.g. Fig.1). It can take up to 4 shots for a sample to reach a 'stable' composition. Rock surfaces have variable amounts of visible. Both Rocknest_3 and Pearson appear in MastCam images to be darker-toned rocks with a thin layer of lighter-toned dust on their surfaces, although only Pearson had visible dust aggregates in RMI images. For these samples, the first 1-2 shots are different from the subsequent 18-19 shots, which are very uniform (Fig. 1). This is in contrast to Goulburn_7 and Stark, which do not appear very dusty in images and whose spectra were variable for 4+ shots. In the case of Goulburn_7, sampling locations 4 and 5 appear variable throughout the 20 first shots. Rocknest_3 and Pearson (Fe-rich) represent a different type of material than Goulburn_7 (conglomerate) and Stark (felsic), and the latter two were scoured by MSL's retrorockets during landing. However, both PCA models and direct comparison of first shots suggest that all rock surfaces are enriched in Mg, Ca, and in some cases H regardless of surface appearance (not shown, confirmed by [9-10]). Only the Goulburn samples lack H in all shots. Of particular interest is Zephyr, which shows both a lack of visible dust and a darker-toned material in spots 4-6. In these locations, Zephyr's composition does not stabilize for ~3-4 shots. Based on these results, we suggest that Stark, Goulburn_7 (points 4 and 5), and Zephyr (points 4-6) may show signs of thin coatings, which may be compositionally related to the dust. This is consistent with results for rock surfaces in the Rocknest region [11], albeit without an observation of Si enrichment.

Dust versus coatings: How to differentiate? Our results are consistent with a single type of material covering rocks of different compositions. This is the signature expected from a single-composition coating. Previous work has shown that in LIBS depth profiles there is often not a sharp transition between a coating and its host rock even if there is a sharp compositional boundary [5, 6]. However, this signature is not unique to coatings alone, since a layer of airfall-deposited dust would produce similar effects. One potential clue that may help to differentiate between these two models is the number of shots required to reach a stable rock composition. Although it is not clear exactly how many LIBS shots are required to remove a thin layer of dust, observations of LIBS analysis craters suggest that loose material is easier to ablate than a coating (and thus requires fewer shots to remove). Laboratory work will elucidate this issue. Additional experiments with the MSL payload could also include a campaign to LIBS/image a location three times: once before brushing, once after brushing, and once after drilling. This would provide information about dust thickness, uniformness, and chemistry, as well as allowing for a measurement of 'fresh' material beyond the reach of a LIBS depth profile.

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JPL: CL#13-0022. LANL: LA-UR-13-20035