

HIGH CALCIUM PHASE OBSERVATIONS AT ROCKNEST WITH CHEMCAM S. M. Clegg¹, N. Mangold², S. Le Mouelic², A. Olilla³, R. Anderson⁴, D.L. Blaney⁵, B. Clark¹⁰, A. Cousin^{8,1}, M.D. Dyar⁶, ¹²B. Ehlmann, C. Fabre⁷, O. Forni⁸, J. Lasue⁸, P.-Y. Meslin⁸, S. Schroder⁸, J.-B. Sirven⁹, ¹¹D. Vaniman, S. Maurice⁸, and R.C. Wiens¹ and the MSL Science Team, ¹Los Alamos National Laboratory, USA (sclegg@lanl.gov), ²Laboratoire de Planétologie et Géodynamique de Nantes, France, ³University of New Mexico, USA, ⁴USGS, Flagstaff, USA, ⁵NASA Jet Propulsion Laboratory / California Institute of Technology, ⁶Mt. Holyoke College, USA, ⁷Univ. Nancy, France, ⁸IRAP, Toulouse, France, ⁹CEA, France, ¹⁰Space Science Institute, USA., ¹¹Planetary Sciences Institute, USA., ¹²California Institute of Technology, USA.

Introduction: The ChemCam instrument probed locations on several samples that recorded relatively high Ca concentrations compared to other locations probed on the same rock or soil. Specifically, these high calcium phases were observed on Pearson (sol 60), Epworth (a soil on sol 72) and Rocknest_6a (sol 87). Pearson and Rocknest_6a were rocks, measured with a 3x3 matrix of laser shots as depicted in Figure 1, while Epworth was a soil that was probed with a 1x5 line. This paper reports the ChemCam elemental compositions of these locations with special attention to the high calcium geochemistry.

The ChemCam instrument on the Curiosity rover consists of a remote Laser-Induced Breakdown Spectrometer (LIBS) and a remote micro-imager (RMI). [1,2] The LIBS instrument is fundamentally an elemental analysis tool capable of probing samples up to 7m from the mast of the rover. The RMI is integrated into the telescope and records high resolution context images.

Investigation Details: The Pearson, Epworth, and Rocknest_6a samples were 3.569m, 2.258m, and 2.542m from ChemCam on the Curiosity mast. Each location was probed with 30 laser shots using the maximum 14mJ/pulse laser energy. The first 5 ChemCam LIBS laser shots generally contain emission from surface dust in addition to the underlying rock or soil and the contribution from the dust is not part of this investigation. The LIBS spectra from the final 25 laser shots were averaged from each of the 23 locations probed.

Elemental compositions were extracted from the 23 averaged LIBS spectra using the ChemCam Partial Least Squares 2 (PLS2) routine and 60 geochemical standards [3,4]. Initial processing involved removing the background, spectral noise and Bremsstrahlung continuum as well as wavelength recalibration and resampling into a common set of spectral bins.

Results: Figure 2 shows key wavelength regions of the LIBS spectra for a subset of locations probed on each sample. The left half of Figure 2 includes the prominent 393 nm and 396 nm calcium lines as well as the 422 nm Ca line and the 404.5 nm Fe emission line. The right half of Figure 2 contains additional Ca lines as well as the 589 nm Na, 766 nm and 769 nm K, and 777 nm O lines. [5]

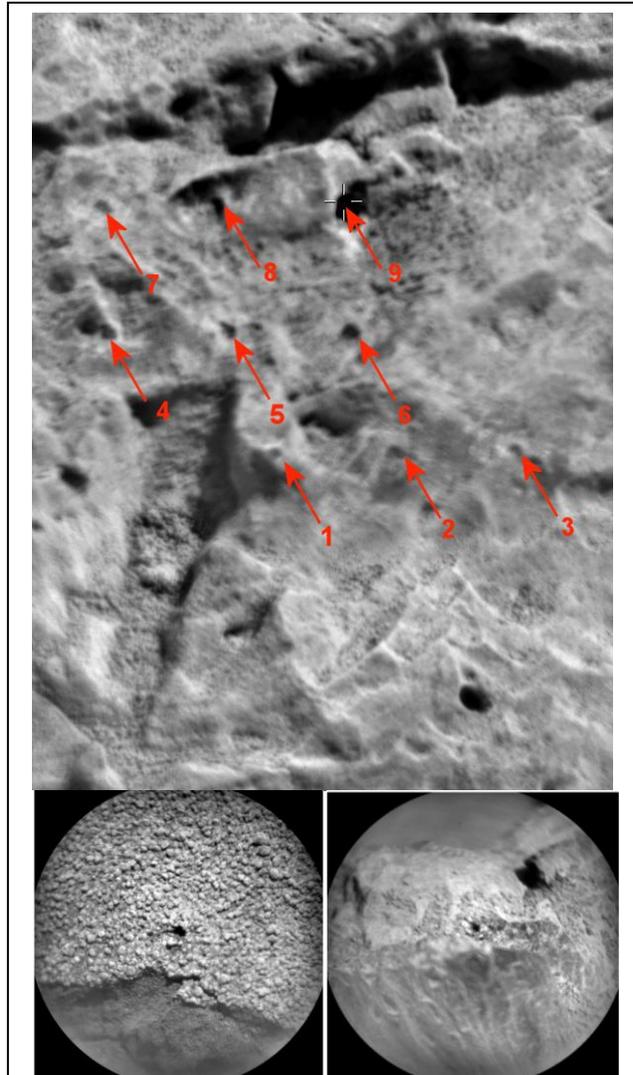


Figure 1: The RMI images of Pearson (top), Epworth soil (left), Rocknest_6a (right) collected with the standard 50ms exposure time. The arrows in the top image point to the LIBS analysis spots.

The latter spectral region contains a broad emission that we interpret as CaO (605nm) molecular emission feature. When LIBS spectra contain elevated concentrations of certain elements, such as Ca or C, simple diatomic or triatomic species can form in an electronically excited state and are observed in the LIBS spectra. The CaO emission lines observed in Figure 2 are an obvious indication that several Ca-rich

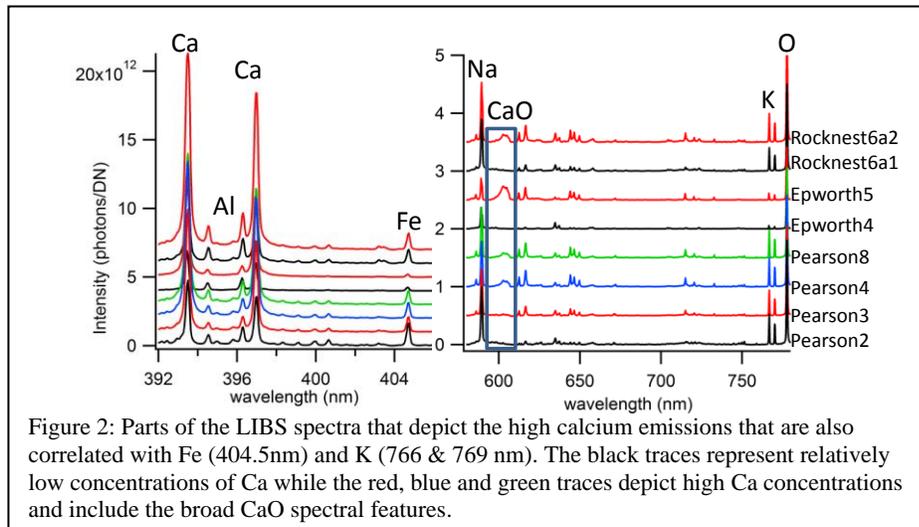


Figure 2: Parts of the LIBS spectra that depict the high calcium emissions that are also correlated with Fe (404.5nm) and K (766 & 769 nm). The black traces represent relatively low concentrations of Ca while the red, blue and green traces depict high Ca concentrations and include the broad CaO spectral features.

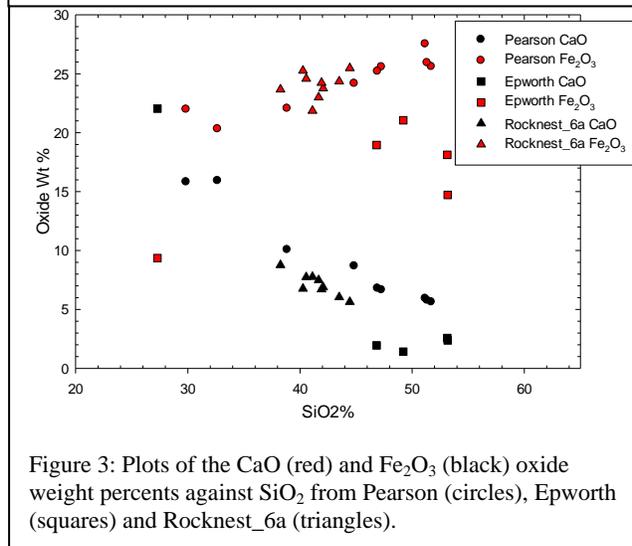


Figure 3: Plots of the CaO (red) and Fe₂O₃ (black) oxide weight percents against SiO₂ from Pearson (circles), Epworth (squares) and Rocknest_6a (triangles).

locations on Pearson, Epworth and Rocknest_6a were probed. Specifically, Pearson 3, 4, 8, Epworth 5, and Rocknest_6a 2 all contained elevated Ca concentrations relative to the other locations probed.

Discussion: Inspection of 23 ChemCam LIBS spectra shows several instructive correlations between the major elements, some of which can be observed in Figure 2. For example, there is a strong, nearly linear anti-correlation between CaO and SiO₂ that is consistent in the Pearson and Rocknest_6a as well as the Epworth soil (Figure 3). In contrast, the Fe₂O₃ concentration increases with increasing SiO₂ and decreasing CaO. Similar trends were observed with Al₂O₃, MgO, and Na₂O that are also anti-correlated with CaO in Pearson, Epworth and Rocknest_6a.

These results show that the Ca-rich phase(s) are not silicates and require a missing anion in the chemical balance. Carbon is visible but at the same level as the atmospheric CO₂ contribution observed in all spectra

acquired to date, thus discarding carbonates as the most likely candidate. Unfortunately, LIBS has relatively high detection limits for S, P and Cl leading to uncertain identification of putative phases such as Ca-sulfates, Ca-phosphates and Ca-chlorides perchlorates. The H spectral signature suggests structural water is not present, thus eliminating hydrated phases such as gypsum.

At Rocknest, the LIBS chemistry mass balance analysis indicates that CaO is present at 30-40% in the Ca-rich phase, suggesting anhydrite (CaSO₄), phosphates such as apatite (Ca₅(PO₄)₃), Ca-perchlorate (CaClO₄). In addition, APXS found 1-2% higher sulfur (up to 5% total SO₃) than previous samples with relatively low (<1%) P and Cl.[6] SAM found perchlorates in low amount in soils, but thermal profiles suggest Mg-perchlorates, not Ca-perchlorates [7]. ChemMin analysis detected anhydrite in the soil at minor abundances but did not detect phosphates or perchlorates. This collection of data suggests that this phase is either anhydrite or apatite, while Ca-perchlorate is much less likely.

Anhydrite and apatite can form in different ways: (1) As a minor igneous phase formed in volatile-rich igneous rocks (2) As a precipitate from fumaroles around hot degassing volcanic material (3) As an aqueous low-temperature precipitate either directly at low water activity or indirectly by later dehydration (4) As a hydrothermal precipitate.

Further analyses of the geological context at Rocknest and additional LIBS data processing will help us to distinguish the origin of this specific phase and understand the origin of volatiles involved. More recent ChemCam investigations along the traverse from Rocknest to Yellowknife continue to detect similar Ca-rich phases including hydrated and anhydrous sulfates and a more complete understanding of the geochemical origin of these phases is beginning to emerge.

References:[1] Wiens et al. Space Science Review, 170, 167, 2012, [2] Maurice et al. Space Science Review, 170, 95, 2012, [3] Clegg et al. Spectrochimica Acta B, 64, 79, 2009, [4] Wiens et al. ChemCam Calibration, in preparation, [5] Cousin et al. Spectrochimica Acta B, 66, 805, 2011 [6] Schmidt, M. et al., this conf [7] Archer, P.D. et al. this conf.