TRACE ELEMENT (STRONTIUM, BARIUM, RUBIDIUM AND LITHIUM) ANALYSES BY CHEMCAM FOR THE FIRST 360 SOLS IN GALE CRATER, MARS.
A. M. Ollila[1], H.E. Newsom[1], R. C. Wiens[2], S. Maurice[3], V. Sautter[4], N. Mangold[5], B. Clark[6], D. Vaniman[7], J. G. Blank[8], J. Bridges[9], A. Cousin[2], R. L. Tokar[7], O. Gasnault[3], O. Forni[3], J. Lasue[3], R. Anderson[10], S. M. Clegg[2], M. D. Dyar[11], C. Fabre[12], N. Lanza[2], A. Rosen-Gooding[13] and the MSL Team. [1]Department of Earth and Planetary Sciences, Institute of Meteoritics, Univ. of New Mexico, MSCO3 2050, 1 University of New Mexico, Albuquerque, New Mexico USA 87131, aollila@unm.edu, [2]Los Alamos National Laboratory, Los Alamos, NM, USA [3]IRAP, Toulouse, France, [4]MNHN, Paris, France, [5]LPGN, Nantes, France, [6]SSI, Boulder, CO, USA [7]PSI, Tucson, AZ, USA, [8]NASA Ames, Moffett Field, CA, USA, [9]Space Res. Center, Univ. of Leicester, UK, [10]USGS, Flagstaff, AZ, USA, [11]Mt. Holyoke College, South Hadley, MA, USA, [12]G2E, Nancy, France, [13]Albuquerque Academy, Albuquerque, NM, USA.

Introduction: The Mars Science Laboratory (MSL) rover, Curiosity, has been exploring Gale crater, Mars since Aug 2012, seeking evidence of past or present habitable environments. Its Chem-Cam package includes a Laser-Induced Breakdown Spectroscopy (LIBS) instrument to provide chemical data on geologic targets and a remote micro-imager (RMI) for context imagery [1]. LIBS is a spectrochemical atomic emission technique in which a pulsed laser is focused on a surface, ablating the surface to form a plasma of excited species that emit at characteristic wavelengths as the plasma cools. Repeated laser pulses on one location removes dust and probes up to 1 mm into the rock's surface. ChemCam can detect most major elements and many trace elements. Quantitative models for Sr, Ba, Rb and Li are presented in [2], as are results for the first 100 sols of analyses of Gale crater. This work is an update to that study for analyses conducted through sol 360.

Trace Element Modeling: A detailed discussion of the quantitative modeling for these elements is given in [2] and is summarized here. Sr abundances are obtained from a Partial Least Squares (PLS) model using an igneous matrix type training set. The Ca-sulfate veins are the primary analyses of a different matrix and therefore Sr abundances for these targets are obtained from a PLS model that contains all sample types including Ca-sulfates. A specialized model for Sr in Ca-sulfate is being developed. The primary Ba peak suffers from interference by Si and Ti emissions, and the Si emission is very energy dependent. Differences in energy in the calibration set and typical ener-

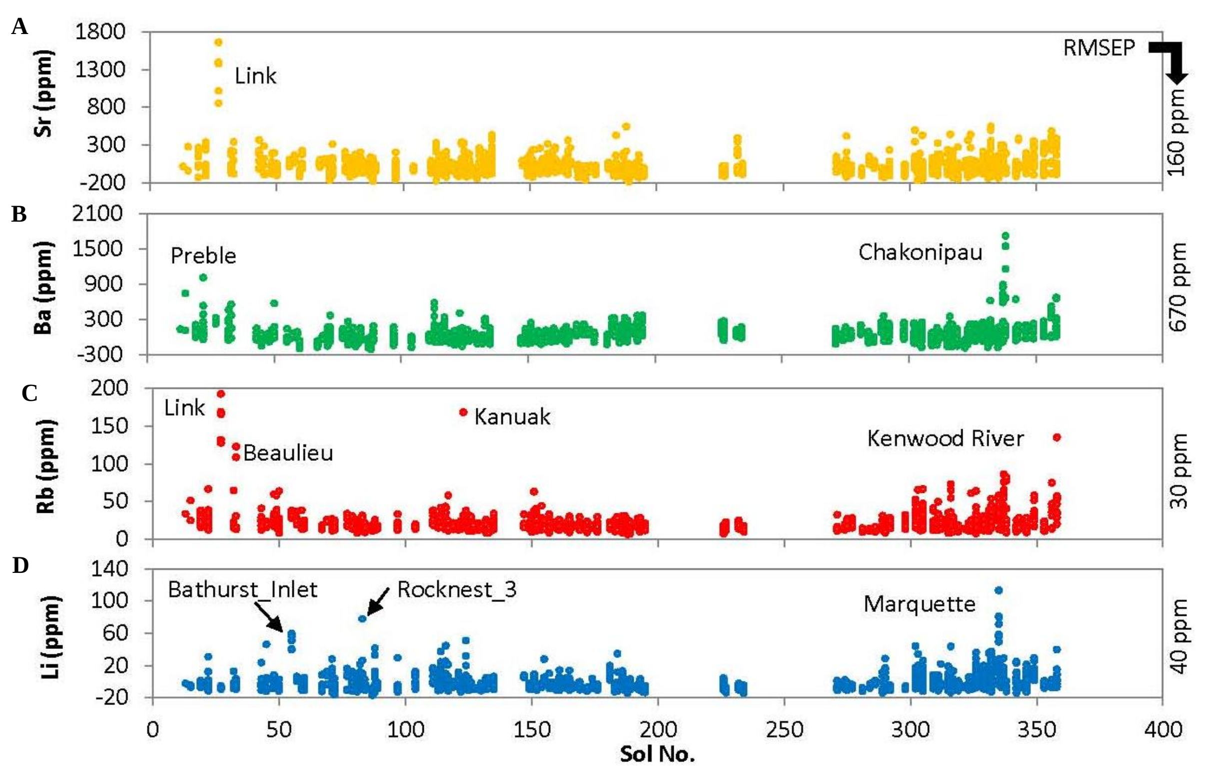

Fig. 1 Sr (a), Ba (b), Rb (c), and Li (d) abundances for the first 360 sols of ChemCam analyses in Gale crater. The RMSEP for each model is listed on the right. Targets with significant enrichments are labeled on each plot.

gies used on Mars can result in overestimates in Ba on Mars due to an enhanced Si peak. Careful fitting of the Ba, Si and Ti peaks can allow for a more rigorous analysis and thus final results will use a univariate calibration method. However, while Ba peak areas for the Mars data are being obtained, a PLS model is used for Ba quantification. Ba abundances for selected targets discussed in the results section have been cross-checked for consistency with the univariate model. Rb abundances are obtained from a PLS model. The close proximity of the primary Rb peak to a large O peak interferes with estimating low abundances of Rb (<30 ppm). Li abundances were obtained from a PLS model. This model tends to give slightly negative estimates at low abundances. Errors are assessed using the Root Mean Square Error of Prediction (RMSEP) are are: Sr (ign. matrix) - 160 ppm, Sr (all matrix) - 430 ppm, Ba- 670 ppm, Rb - 30 ppm, and Li - 40 ppm.

Results: The highest observed Sr through sol 360 occurs in felsic light-toned clasts in the conglomerate Link described in [3]. The analysis points on Link contain 800-1800 ppm Sr (Fig. 1a) and are also enriched in Rb (>100 ppm). While ChemCam has analyzed additional light-toned clasts in other rocks since Link, including conglomerates, no other targets have more than ~550 ppm Sr. Elevated Sr is also observed in the Ca-sulfates found in the Sheepbed mudstone relative to the mudstone itself. Additional calibration models specific to the Ca-sulfate matrix are needed to accurately constrain the Sr abundances but there is likely >400 ppm Sr present in most of the veins.

Several targets early in the traverse and toward the end of the first 360 sols contain Ba > 600 ppm. The Ba peak is difficult to discern in ChemCam spectra due to interfering Si and Ti peaks. However, a clear identification of Ba was observed in a buried pebble in the Akaitcho sand formation with ~1000 ppm Ba when the laser shots that sampled soils are excluded. On Sol 338, ChemCam sampled a light-toned rock named Chakonipau [4] and 4 of the 5 locations showed enrichments in Ba, on the order of 1500-2000 ppm. These points are also somewhat enriched in Rb (~80 ppm).

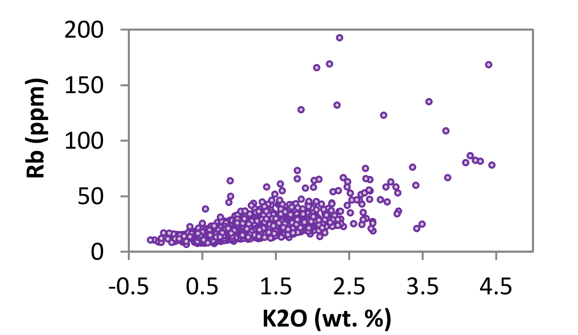

Fig. 2 Correlation between Rb & K_2O abundances.

There is little correlation between Sr and Ba, and 2 primary trends are observed in the extreme cases with Link defining a low Ba, high Sr trend and Chakonipau defining a high Ba, low Sr trend. No discerable Ba is present in the Ca-sulfate veins

Link remains the highest in Rb content through 360 sols (Fig. 1c). However, in point 3 of the Kanuak soil analysis, a buried pebble sampled by ChemCam contains a similar amount of Rb (170 ppm). Pebbles in the Beaulieu soil and one point in the conglomerate Kenwood River have Rb >100 ppm. Rb abundances generally correlate with K abundances (Fig. 2).

Several instances of relatively high Li have been observed in the first 360 sols (Fig. 1d). The highest Li is in a possible bedrock target called Marquette analyzed on sol 335. Seven of the 10 analysis locations show enrichments in Li (>50 ppm) and point 3 shows a marked increase in Li over the 30 shot depth profile (Fig. 3). Li in point 3 is positively correlated with Ca, Mg and Fe and inversely correlated with K, Na, Si, Al, and H. Several other locations show a sharp drop after an initial increase following dust removal.

Conclusions: The high Sr abundances in Si-rich light-toned clasts in conglomerates may imply the presence of plagioclase feldspar. Sr is present in Ca sulfate veins at abundances lower than terrestrial analogues [5] but these values will be revised using a matrix-matched calibration suite. High Ba in a Si-rich light-toned rock is consistent with alkali feldspar. Elevated Rb in both Sr and Ba rich material is also consistent with feldspar. Li is enriched in several locations on a dark-toned rock called Marquette. Changes in composition with depth and between analysis location on this rock are complicated and additional work is needed to determine the Li-bearing phase. It is possible the Li is in pyroxene, Mg/Fe clays, or salts.

References: [1] Wiens et al., 2013, *Spectrochim. Acta B*, 82, 1-27 [2] Ollila et al., 2013, *J. Geophys. Res.*, in press [3] Williams et al., 2013, *Science*, 340, 1068-1072 [4] Sautter et al., 2014, LPSC. [5] Kah et al., 2001, *Precambrian Res.*, 111, 203-234.

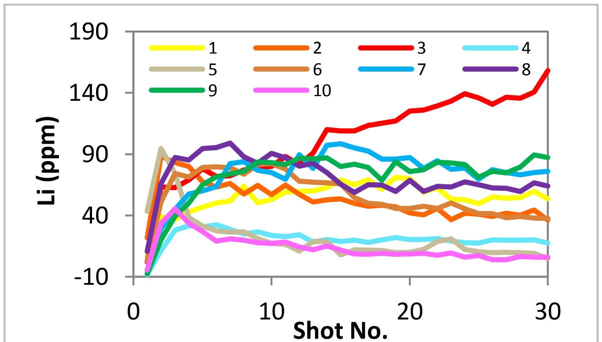

Fig. 3 Li depth profiles in Marquette