

STRONTIUM CALIBRATION FOR CHEMCAM IN GALE CRATER, MARS. J. M. Williams¹, A. M. Ollila¹, H. E. Newsom¹, S. Gordon¹, R. C. Wiens², S. M. Clegg², L. C. Kah³ and the MSL team, ¹Institute of Meteoritics, Department of Earth and Planetary Sciences, Albuquerque, NM, USA, (josh505@unm.edu) ²Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545, U.S.A. ³Dept. of Earth and Planet. Sci., Univ. of Tenn., Knoxville, TN,

Introduction: The ChemCam instrument is on the mast of the Mars Science Laboratory (MSL) Curiosity rover. ChemCam consists of a Laser Induced Breakdown Spectrometer (LIBS) that analyzes targeted elements at a distance and an integrated Remote Microscopic Imager (RMI) to provide context of the LIBS spectra location. LIBS can detect all major elements (Si, Ca, Mg, Al, K, Na, Ti, and Fe), several minor elements (H, C, N, P, S, Cl, and Mn), and many trace elements (Li, B, Rb, Sr, Ba, Cr, Ni, Cu, Zn, As, Cd, and Pb). Fluid mobile elements such as Strontium are important to better understand diagenetic alteration processes on Mars. Quantifiable abundances of Sr can provide diagnostic tools for understanding processes of fluid rock interaction mechanisms, diagenesis, and possible groundwater evolution in Gale crater, Mars. It is therefore vital to be able to accurately quantize Strontium abundances with MSL's LIBS laser. The purpose of this study is to further calibrate Sr abundances and to improve standard calibration as measured by the ChemCam in Gale Crater, Mars, by comparing LIBS data collected at Los Alamos Labs of terrestrial analogs with ICP-MS analysis of the same terrestrial analogs.

Terrestrial Analogs: A suite of terrestrial analogs were obtained from the 1.2 Ga carbonate-evaporate succession of the northern Baffin and Bylot Islands. The samples are from [1]the oldest preserved, laterally extensive, bedded marine CaSO₄ evaporates in the ~1.2 Ga Grenville and Bylot Supergroups. The 1.2 Ga Society Cliffs Formation (Bylot Supergroup, northern Baffin Island) consists of ~720 m of peritidal carbonates, evaporates and minor siliciclastic rocks. Evaporites occur predominantly in the lowermost 300 m of the Society Cliffs Formation, where gypsum beds (1-250 cm thick) constitute up to 15% of the exposed strata. Stratigraphic and sedimentologic constraints, as well as isotopic (C, O, and Sr) and elemental (Ca, Sr, Na, K, Ba) compositions of evaporates and associated carbonates, indicate a marine origin for Society Cliffs gypsum. The inferred rapidity of isotopic change requires a marine sulfate reservoir significantly smaller than that of the modern ocean. Previous stratigraphic (Kah, in press) and geochemical investigations (Kah et al., 1999; Kah, 2000) of Society Cliffs carbonate rocks has helped constrain environments of deposition and

diagenesis, and is a good analog to demonstrate our ability to infer primary and secondary geochemical processes.

Methods: The samples have been crushed and powdered at the University of New Mexico. The concentrations of major and trace elements (Ca, Mg, Sr, Mn, Fe; plus Ba, Na, K in the terrestrial analog gypsum samples) will be measured at the University of Tennessee, Knoxville using a Perkin-Elmer inductively-coupled plasma-atomic emission spectrometer (ICP-AES) fitted with a micro-concentric nebulizer and calibrated to a series of gravimetrically determined standards. Aliquots of the samples have been pressed into pellets for LIBS analysis at Los Alamos in the near future.

The LIBS technique has shown consistency in achieving its mission goals of providing quantitative elemental compositions of major and trace elements [2]. ChemCam LIBS observations on Mars are normally taken as a two-dimensional raster of laser spots with 30 to 50 nanoseconds-long laser pulses per shot; however, the Nd:KGW laser can shoot up to 1000 shots at one location and profile up to 1mm of depth into a rock. Spectra are returned through a telescope in the mast of the rover, where the laser is also located, and transmitted to three spectrometers ranging in wavelength from 240 to 850 nm. Spectra are analyzed using multivariate analysis (MVA) techniques such as partial least squares (PLS) and principal component analysis (PCA) to account for chemical matrix effects related to the plasma and coupling efficiency [3]. Multiple laboratory tests of the LIBS system have been conducted to verify its ability to characterize terrestrial rocks using averages of laser shots with a spatial resolution on the order of 400 microns. The LIBS instrumentation at LANL is designed to simulate the ChemCam instrument on MSL and laboratory conditions mimic martian conditions with a chamber filled with 7 Torr CO₂. Samples consisting of pressed powder pellets are placed in the chamber 1.6 m from the laser and rotated by hand to target ten different spots. typically 50 shots will be fired at 95 A and 12 mJ per pulse at a repetition rate of 3 Hz. Spectra will be collected and processed in the same way as ChemCam LIBS spectra.

Conclusions: The samples in this study consist of the 1.2 Ga carbonate-evaporite succession, from the northern Baffin and Bylot Islands. The gypsum samples cover a broad range of bulk chemistries, some of which may be present on Mars. Analysis of the samples by LIBS using the ChemCam simulator for comparison with ICPMS data will allow for a better understanding of the LIBS calibration and matrix effects for the fluid mobile element strontium.

References: [1] Kah, L. C. et al. (2000) *Precambrian Research*, 111, 203-234. [2] Wiens R. C. et al. (2012) *Space Sci Rev*, 170, 167-227. [3] Clegg S. et al. (2009) *Spectrochim. Acta Part B*, 64, 79-88.