SIMULATED CHEMCAM LABORATORY INVESTIGATIONS OF EAST AFRICAN RIFT SEDIMENTARY SAMPLES.

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Introduction: ChemCam is one of the instruments selected for the Mars Science Laboratory Rover. It is the integration of a Laser-Induced Breakdown Spectrometer (LIBS) and a Remote Microimager (RMI). The LIBS instrument will probe samples up to 9 meters from the top of the rover mast to determine the elemental composition. The RMI will collect images of the samples probed by LIBS.

LIBS involves focusing a high power laser onto the surface of the sample. The laser ablates some of the material on the sample surface generating an expanding plasma containing electronically excited atoms, ions and small molecules. These species emit light as they relax to lower electronic states at wavelengths indicative of the species in the sample. Some of this emission is collected with a telescope, directed into a dispersive spectrometer and recorded with a charge-coupled device (CCD) detector.

Because it is likely that ChemCam will encounter sedimentary rock types, a laboratory remote LIBS experiment was designed to probe a suite of diverse sedimentary samples with igneous rock precursors [1]. Samples from the East African Rift (EAR) were chosen because rift valleys are prominent features on the surfaces of both Mars and many continents of Earth. Valles Marineris (~8000x200x5 km) dominates the face of Mars, and on Earth the EAR (~6000x150x3 km) is by far the largest modern rift system. Both rifts are formed by extensional tectonics producing thick sequences of basalt flows and volcaniclastic sediments and expose significant sections of planetary crusts.

Geological Background: The EAR is centered in the low latitudes (tropics) and because of the low elevation of the EAR floor, the rift has a localized climate system that is dominated by arid weathering and erosion where evaporation is 4-5 times higher than precipitation. The regional settings of both EAR and Valles Marineris show morphological evidence of arid landscapes: playa lakes and ephemeral rivers and groundwater-fed discharges. The EAR soils (inceptisols) and lakes that form in evaporative basins precipitate sulfates (gypsum and anhydrite), chlorides (halite and sylvite) and trona. In Valles Marineris, and the near-equatorial region of Mars around it, the climate is known in less detail, but is dominated by dryland processes.

Volcanism in the EAR ranges in composition from basalt to andesite to trachyte and their alkaline/peralkaline equivalents[2]. Composition inferred from orbital observatories (i.e. spectral data) suggest basalts on surfaces of Mars within 40º of the equator. Spectral data from Mars Express and the Mars Reconnaissance Orbiter (MRO) of martian regolith suggests large areas of phyllo-silicates (clay) and evaporites. Analysis of the soil samples collected by the Viking landers in 1976 indicate iron-rich clays consistent with weathering of basaltic rocks [3]. Weathering and erosion in both sites have produced a valley floor covered with fans of volcaniclastic debris derived from these lavas.

In short, the EAR system may be a good Earth analogue for areas on Mars suggesting rifting, as well as

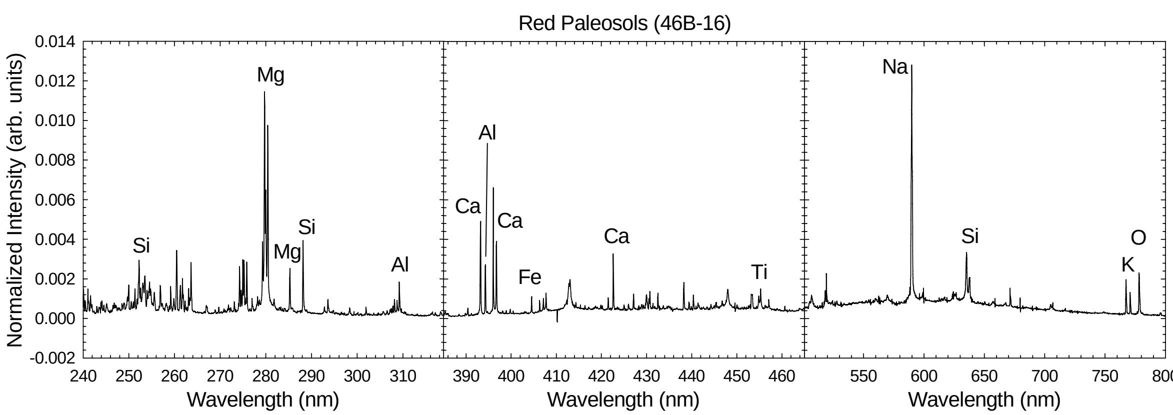

Figure 1: Representative LIBS spectra (from three different spectrometers) from a red paleosol (46B-16) at a 9m standoff distance. Most LIBS spectra are similarly spectrally rich and many of the major element emission lines are identified.

for martian surface sediments, in general, in terms of tectonics, petrology, and climate. Of course, there are differences in weathering processes related to liquid water availability, temperatures, redox conditions, etc., which are obviously different now and may have been so earlier in Martian history, the overall similarities make these a good Mars analog for our current purposes.

Samples: The experiments involved probing 17 sedimentary samples from Olduvai Gorge, Tanzania in the EAR, including waxy claystone, tuff and tuffaceous sediment, lapilli-rich claystone, calcareous lithofacies, silty claystone, and red paleosols. These samples were ground into rock powders and pressed into ~30mm pellets. Eight rock powder standards were also used to calibrate the experimental setup and include basalts (GBW 07105, GUW BM, BHVO-2, GSR-3), andesites (Ja-1 AGV-2), and dolomites (NBS 88b, JDo-1). These standards were also pressed into 30mm pellets.

Experimental Details: These experiments were designed to replicate the ChemCam instrument performance but did not involve either the flight or engineering models. The LIBS plasma was generated by focusing a Nd:YAG laser operating at 1064nm and 10Hz repetition rate onto the sample surface. The laser pulse energy was 17±1mJ/pulse which is coincides with the 15-20 mJ/pulse ChemCam will deliver on target. Some of the LIBS plasma emission was collected with a 89mm telescope which is slightly smaller than the 110mm ChemCam telescope. The emission collected with the telescope was directed through a 1m long, 300μm, 0.22NA solarization-resistant optical fiber and into one of three Ocean Optics HR2000 commercial spectrometers. The three spectrometers recorded the emission over the 223.40 – 325.97nm (UV spectrometer), 381.86 – 471.03nm (VIS spectrometer) and 494.93 – 927.06nm (VNIR spectrometer). The spectrometer exposure time was 1 second and monitored the emission of 10 laser shots per exposure. Each recorded spectrum was the average of 5 spectra which represents 50 total laser shots. Each sample was probed in 5 different locations.

ChemCam will probe samples between 1.5 and 9m from the mast of the rover. The samples probed in these experiments were positioned 9m from the telescope. LIBS is also very sensitive to the atmospheric pressure and performs optimally under the reduced martian surface pressure. The samples were placed in a vacuum chamber filled with 7 Torr CO_2 to simulate the Martian surface pressure.

Results: Figure 1 shows representative spectra from one of the EAR red paleosols, sample 46B-16; its major element composition as determined by XRF is given in Table 1. LIBS spectra are typically structurally rich containing multiple emission lines for each element as depicted in the figure.

Table 1. Major Element Composition of 46B-16

Oxide	Atomic Fraction		%Δ
	Known	LIBS	
SiO_2	49.98	50.21	0.45%
Al_2O_3	15.21	14.82	2.55%
MgO	3.64	4.47	21.04%
CaO	0.943	1.35	43.49%
Na_2O	5.08	5.40	0.85%
K_2O	2.22	2.53	13.99%
TiO_2	1.55	1.55	0.01%
	[illegible]		

Multivariate analysis (MVA) was employed to calibrate and analyze the LIBS spectra [4]. First, Partial Least Squares (PLS) analysis was used to generate a calibration model using four of the standards (JA-1, GBW 07105, NBS 88b, GUWBM) and six of the EAR samples. Principal Components Analysis (PCA) was used to identify the spectral variations in all of the samples.

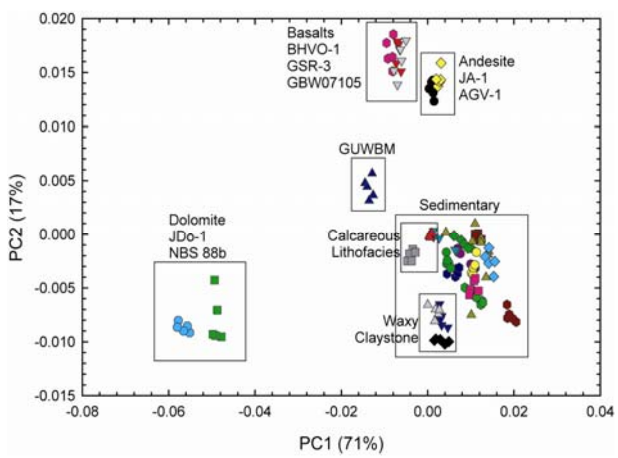

Figure 2: Principal Components Analysis (PCA) for all of the samples and standards explored in the paper. PCA can be used to develop a predictive model for rock types. PC1 and PC2 are dominated by variations in Ca, Mg, Na and Ca, Mg, Fe, respectively

A PCA plot is depicted in Figure 2 where PC1 and PC2 describe 71% and 17% of the variations in the spectra. PCA can clearly distinguish the standards (basalts, andesites, and dolomites) from one another as well as the EAR sedimentary samples. PCA analysis such as this can be employed to predictively identify the sample rock-type [4].

References: [1]Ashley, G.M., Driese, S.G. (2000) *J. of Sedimentary Res.*, *70*, 1065-1080. [2] McHenry, L.J. (2005) *Stratigraphy*, 2, 101-115.. [3] Francis, P. (1993) Volcanoes: A Planetary Perspective, Clarendon Press, 443 p. [4] Clegg, S. et al., *Spectroch.*, submitted.