

**FABRICATION OF SULFATE-BEARING CERAMIC CALIBRATION TARGETS FOR THE CHEMCAM LASER SPECTROSCOPY INSTRUMENT, MARS SCIENCE LANDER.** D. T. Vaniman<sup>1</sup>, S. Clegg<sup>2</sup>, N. Lanza<sup>3</sup>, H. Newsom, R.C. Wiens<sup>4</sup>, and the ChemCam Team, <sup>1</sup>Group EES-14, MS D462, Los Alamos National Laboratory (LANL), Los Alamos, NM 87545 (vaniman@lanl.gov), <sup>2</sup>Group C-CDE, LANL, <sup>3</sup>Institute of Meteoritics, UNM, Albuquerque, <sup>4</sup>Group ISR-1, LANL.

**Introduction:** The ChemCam (chemistry/camera) instrument on the Mars Science Lander (MSL) images outcrop or regolith at high resolution and uses a laser source to generate high-temperature plasma from spots of ~100  $\mu\text{m}$  diameter, at ranges up to ~7 m [1,2]. The lander will carry body-mounted calibration targets consisting of synthetic silicate glasses, a natural volcanic glass (macusanite), and four sulfate-bearing ceramics. The synthetic silicate glasses and the macusanite are highly homogeneous at the scale of laser spot sampling; they are described in detail elsewhere [3]. This abstract describes the fabrication and characterization of ceramic calibration targets.

**Rationale for ceramic targets:** The synthetic and natural silicate glass targets are formed at temperatures that do not retain sulfur. Targets made of sulfate and sulfide minerals were investigated but found unacceptable because of fragility, instability, or inadequate plasma production. Because sulfate-bearing lithologies are important at all potential MSL landing sites, it was decided to prepare low-fire ceramics with firing temperatures below sulfur volatilization (~900-1000 °C).

In addition to this thermal requirement, a secondary goal was to make ceramics based on three major components expected at the potential landing sites: a sulfate mineral, phyllosilicates, and basaltic detritus. The sulfate phase selected was anhydrite, which produces no water on heating and retains sulfur at temperatures to at least 850-900 °C. Phyllosilicate components were selected from Clay Minerals Society source samples of Australian nontronite N Au-2 (representing very iron-rich smectite identified at several localities on Mars[4]) and Georgia kaolinite K Ga-2 (representing iron-poor kaolinite-group clay minerals identified at some localities[4]). Although these samples were heated to remove water and hydroxyl (see methods below), the refractory chemical constituents remain representative of clay mineralogy. Basaltic detritus was represented by a tholeiitic lava of the Cerros del Rio lava field, NM, that has been used for several years as an internal standard for X-ray fluorescence analyses at Los Alamos National Laboratory. Three of the ceramic targets were based on differing ratios of anhydrite versus basalt mixed with devolatilized N Au-2; the fourth target was composed of equal amounts of basalt and anhydrite mixed with devolatilized K Ga-2. These mixtures are summarized in Figure 1.

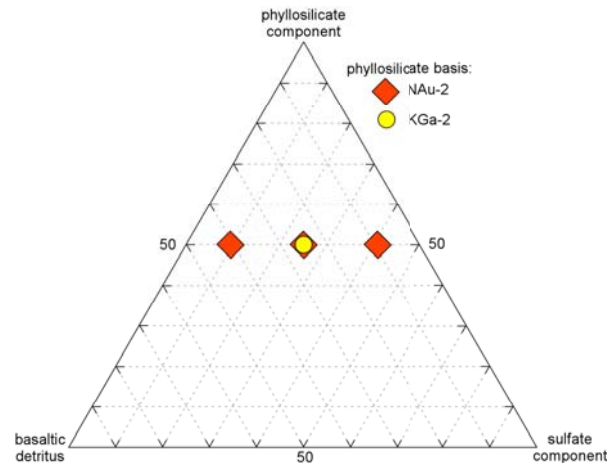


Figure 1: Ternary plot of phyllosilicate, basalt, and sulfate components in four ChemCam ceramic targets as prepared (weight basis).

**Methods:** All components were ground in a tungsten carbide shatterbox or ball mill; mixed and re-ground; and pressed in a SPEX® press at 7 MT before firing to 800 °C. Initial experiments using unprocessed clay minerals produced unacceptable vesiculation and structurally weak ceramics, whether fired with or without a flux (lithium tetraborate). To minimize vesiculation the source clay samples were then pre-fired to 1000 °C to remove all interlayer water and structural OH; this treatment retains the refractory elements characteristic of clay mineral chemistry while greatly reducing vesiculation on subsequent firing. Firing without flux continued to produce weak ceramics. Experiments with varying amounts of lithium tetraborate flux produced optimal hardness (resistance to scratch by steel probe) with ~9 wt% flux added to the primary component mixtures shown in Figure 1. Additions of flux below this amount produced much softer ceramics and higher amounts of flux tend to produce excessive melting and immiscible anhydrite globules.

The firing schedule developed for the ceramics followed preheating overnight at 95 °C by stepwise heating to 800 °C, followed by cooling to room temperature in the closed oven with heat turned off. The firing profile is shown in Figure 2. To meet the size requirements of the target holder on MSL, a special 22 mm diameter piston and cylinder with platens was machined from tool steel. With this press it was found

that splits of <10 g would spall on release of pressure. Therefore pressed masses of ~10 g were pressed, fired, and then cut to final thickness (~5 mm) with an Isomet® saw, using punctilious ethanol as a coolant.

Ceramic targets prepared with these methods had acceptable grain size (~5-15  $\mu\text{m}$ ); vesicles remained, at sizes up to ~100  $\mu\text{m}$ , as shown in Fig. 3, but were deemed acceptable in tests of homogeneity at the scale of laser analysis. Lack of sensitivity to small vesicles is an advantage of the LIBS technique.

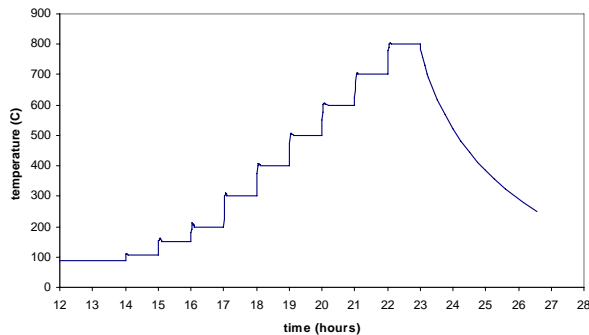


Figure 2: Heating steps and cooling cycle, firing of ChemCam ceramic targets.

**Analysis of ceramics:** Analyses of samples were done by LIBS and by SEM prior to production of the flight units to observe grain size and check for homogeneity. Heterogeneity between LIBS spots was no greater than pressed powder targets typically used as standards in the lab, a finding confirmed later with the ChemCam instrument and with the flight batch of ceramic standards. A typical LIBS spectrum is shown in Fig. 4, with the standard deviation of five analysis spots also plotted. Sulfur peaks are subdued in this spectrum because of detector gain non-linearity that is currently being

fixed. Prior studies indicate that sulfur will be readily detected and quantified [5-8]. Analyses of LIBS calibration against other standards are being done [9]. Analyses of the ceramic standards are also being done by XRF, XRD, and electron microprobe.

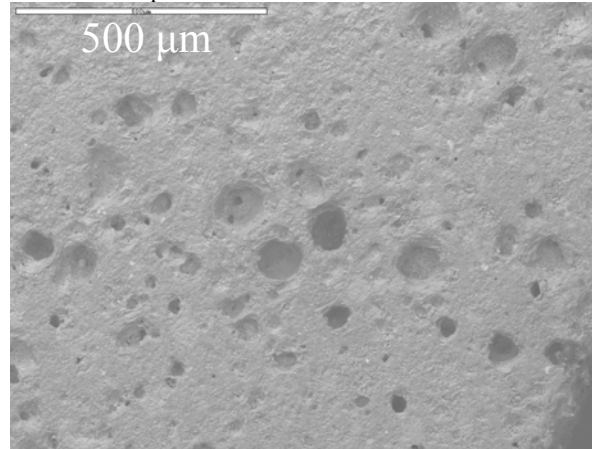


Figure 3: SEM image of NAu-2 medium-sulfur ceramic showing a region of larger voids. Vesicles are generally smaller than the laser spot size and do not effect the analyses.

**References:** [1] Wiens R.C. et al. (2005) *LPS XXXVI*, Abstract #1580. [2] Maurice S. et al. (2005) *LPS. XXXVI*, Abstract #1735. [3] Fabr  C. et al. (2009) this meeting. [4] Mustard J.F. et al. (2008) *Nature* 454, 305-309. [5] Clegg S.M. et al. (2007) *LPS XXXVIII*, Abstract #1960. [6] Dyar M.D. et al. (2008) AGU Fall Mtg., Abstract P43B-1399. [7] Sharma S.K. et al. (2007) *Spectrochim. Acta A* 68, 1036-1045. [8] Sall  B. et al. (2004) *Spectrochim. Acta B* 59, 1413-1422. [9] Wiens R.C. et al. (2009) this meeting.

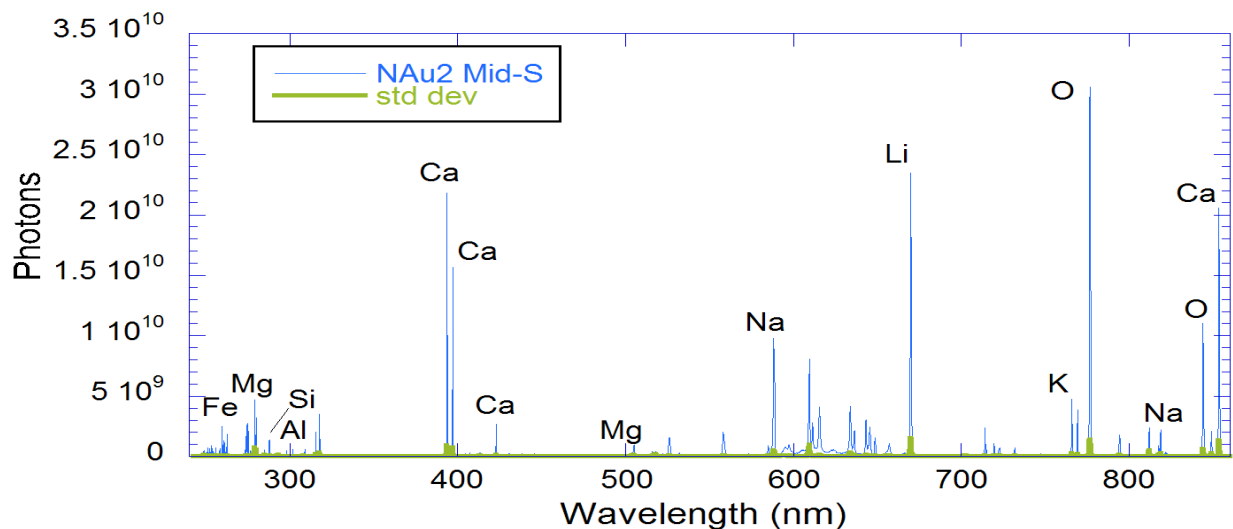


Fig. 4. ChemCam LIBS spectrum and standard deviation of the NAu-2 medium sulfur ceramic target.