Ceramic ChemCam Calibration Targets on Mars Science Laboratory

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Abstract The ChemCam instrument on the Mars Science Laboratory rover *Curiosity* will use laser-induced breakdown spectroscopy (LIBS) to analyze major and minor element chemistry from sub-millimeter spot sizes, at ranges of ~1.5–7 m. To interpret the emission spectra obtained, ten calibration standards will be carried on the rover deck. Graphite, Ti metal, and four glasses of igneous composition provide primary, homogeneous calibration targets for the laser. Four granular ceramic targets have been added to provide compositions closer to soils and sedimentary materials like those expected at the Gale Crater field site on Mars. Components used in making these ceramics include basalt, evaporite, and phyllosilicate materials that approximate the chemical compositions of detrital and authigenic constituents of clastic and evaporite sediments, including the elevated sulfate contents present in many Mars sediments and soils. Powdered components were sintered at low temperature

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(800 °C) with a small amount (9 wt.%) of lithium tetraborate flux to produce ceramics that retain volatile sulfur yet are durable enough for the mission. The ceramic targets are more heterogeneous than the pure element and homogenous glass standards but they provide standards with compositions more similar to the sedimentary rocks that will be *Curiosity's* prime targets at Gale Crater.

Keywords Mars Science Laboratory · ChemCam · Laser induced breakdown spectroscopy · Calibration · Gale Crater · Ceramic · Curiosity

1 Introduction

Mars Science Laboratory (MSL) will begin operations on Mars in the summer of 2012. The MSL mission's highly-capable rover (*Curiosity*) will carry ten instruments, four of which will provide chemical data. First, the Sample Analysis on Mars (SAM) evolved gas and mass spectrometry instrument suite will measure light elements (C, H, O, N, S) and their compounds from collected powders, and also has the capability for isotopic analysis. Second, the CheMin (Chemistry and Mineralogy) X-ray diffraction and fluorescence instrument will, along with diffraction, provide chemical information for elements heavier than silicon in collected powders. Third, the Alpha Particle X-ray Spectrometer (APXS) will provide full chemical analysis for Na and heavier elements in contact samples. Finally, the ChemCam (Chemistry Camera) remote analyzer with a Remote Microimager (RMI) will use laser-induced breakdown spectroscopy (LIBS) to analyze major and minor element chemistry from sub-millimeter spot sizes at ranges of ~1.5–7 m. A detailed description of the ChemCam instrument is provided by Wiens et al. ([this issue](#)). Each of these instruments will be subject to a calibration and characterization regimen and each will carry standard materials to Mars for use in periodic checks of calibration and performance. In this paper, we describe the preparation and properties of the ceramic targets for ChemCam that will be carried on *Curiosity*, along with complementary data for the ChemCam shergottite glass standard that is also described in Fabre et al. ([2011](#)).

The ChemCam instrument uses laser pulses of ~17 mJ to generate light-emitting plasma from rocks or regolith for remote elemental analysis of the emission spectra (Wiens et al. [this issue](#); and Maurice et al. [this issue](#)). Each laser pulse produces a vaporized spot that varies in scale from ~180 μm at 2 m to ~600 μm at 7 m. The range of chemical species measurable by ChemCam covers much of the periodic table up to $Z = 92$ (U), including the biologically important elements H plus C, O, N, P, S—with detection limits varying by element. The standoff analytical capability and rapid data acquisition from multiple analysis spots make ChemCam a formidable asset in determining the nature of *Curiosity's* surroundings and in guiding the rover to the most promising targets for contact analysis.

Included with ChemCam are ten calibration targets, carried in a mount on *Curiosity's* deck. These targets are located 1.56 m from the ChemCam laser, which is mounted on top of the rover's mast (ref. Wiens et al. [this issue](#)). Two of the targets are pure elements (Ti metal and graphitic C), three are synthetic mafic glasses (picrite, norite, and shergottite compositions), one is a natural silicic peraluminous igneous glass ("macusanite" glass from Macusani, Peru), and the remaining four are ceramics. The graphite standard provides calibration of the critical light element C. The glasses provide calibration based on representative basaltic compositions on Mars (picrite, shergottite), an analog of primitive Noachian crust (norite), and for extended calibration a more felsic igneous member (macusanite); the macusanite also contains a small amount of water (up to 0.5 wt.% H₂O).

Fabre et al. (2011) describe the compositional range, target homogeneity, and application to calibration of the natural and synthetic glasses for major elements (Si, Fe, Al, Mg, Ca, O, Na, and K) as well as minor and trace elements (Ti, Sr, Cr, Cs, Ba, Li, Zn, Mn, and Ni). The excellent multi-element homogeneity within each of the glasses makes them the primary calibration targets for ChemCam because they have homogeneity well within LIBS analytical precision no matter where the laser beam is placed. However, the glasses represent igneous compositions while the prime targets for *Curiosity* are sedimentary rocks that may preserve evidence for habitable environments (Grotzinger 2009), as well as soils and sands derived from the sediments. Most important, in light of the expected occurrence of sulfate phases at Gale Crater, the field area that *Curiosity* will explore, is the need for sulfate-bearing standards.

Exploration of sulfate-rich sediments at Meridiani Planum by the Mars Exploration Rover *Opportunity* has revealed extensive deposits of sediments with grain sizes typically 0.1–1 mm, with a sulfate component that includes both sulfate cement and reworked detrital sulfate grains (McLennan et al. 2005; Grotzinger et al. 2006). The sediments of Gale Crater may differ from the cemented sands of Meridiani Planum, but sand-scale granularity and sedimentary porosity are likely to be encountered. Moreover, in addition to sediments it is expected that dune sands and soils with sulfate as well as mafic silicate grains will be found and analyzed by *Curiosity*. These issues were common to all of the candidate MSL field sites at the time that calibration targets for ChemCam had to be prepared, but of all candidate sites the Gale Crater location has the most extensive and complex sulfate story. It is therefore particularly important that *Curiosity* have sulfate-bearing calibration targets. The ceramic targets are similar in chemical composition to an evaporite with mafic silicate detritus and clay minerals. As such the ceramics provide a closer chemical approximation of regolith and sediments expected at Gale Crater, although they have inherent heterogeneity due to their granular nature.

Sulfate analysis will be a major goal of MSL, but so too is the analysis of silicate phases derived from aqueous alteration of mafic igneous rocks. The original mission requirements for ChemCam included a desire that LIBS calibration targets have at least one sample representative of each major rock unit expected to be encountered, including basalt, andesite, and a basalt alteration product, as well as a sulfate. The basalt requirement is covered by the basaltic glasses and the macusanite glass provides a compositional member that extends to a silica range beyond andesite. Missing from the homogeneous glass calibration targets are sulfates and alteration products of basalts. However, these components are critical for meeting the mission's objectives to evaluate habitability.

Sulfates and phyllosilicates both occur at Gale Crater (e.g., Milliken et al. 2010). Several clay minerals have been identified on Mars by spectral signatures detected from orbit. Most identifications are of 2:1 smectites or mixed-layer clays, particularly nontronite, saponite, and chlorite as well as 1:1 aluminous phyllosilicates such as kaolinite (Milliken and Bish 2010). Clay minerals provide evidence of past hydrous systems and water is critical to habitability. Similarly, sulfate minerals identified on Mars (principally Mg, Ca, and Fe sulfates) provide evidence of past hydrous environments. Sulfate phases appear to fill a geochemical role in Mars aqueous surface processes that is assumed by carbonates in the dominant aqueous geochemical cycle on Earth (e.g., McLennan and Grotzinger 2009; King and McLennan 2010). Thus, in addition to providing igneous calibration targets, the ChemCam team created additional ceramic targets that include Mars-like clay minerals (nontronite and kaolinite) as well as a sulfate. All the on-board targets will be used in combination with data acquired with ChemCam before launch, as well as data from *Curiosity*'s other instruments, to examine elemental concentrations in Mars surface materials.

1.1 Preparation Methods and Selection of Target Compositions

Durability is a problem when trying to incorporate a clay mineral or a sulfate phase into a solid analytical target that will be exposed to the martian environment. Clay minerals are soft, and many gain or lose water as humidity changes, swelling or contracting in the process. Studies of smectite hydration at Mars surface conditions indicate that swelling cycles may occur on a daily basis (Bish et al. 2003). Most sulfate minerals are also soft and many occur in varying hydration states that also change with temperature and humidity. For these reasons, calibration targets were created with (1) a clay mineral component that has been processed in a manner (heating to 1000 °C) that prevents hydration/dehydration cycling yet preserves the anhydrous chemical composition and (2) a relatively stable sulfate component. Past missions have shown that sediments on Mars incorporate a significant amount of basaltic detritus (e.g., Toulmin et al. 1977; McLennan et al. 2005); therefore we have included a basaltic component in these targets. The clay samples chosen were Fe-rich smectite (nontronite) and an aluminous clay mineral (kaolinite). Most of the ceramics use the nontronite, which is expected at Gale Crater (Milliken et al. 2010), but kaolinite was used in one target to extend compositional range to sediments that include an aluminous clay mineral. The aluminous ceramic composition was selected in part for the candidate MSL site at Mawrth Vallis, where abundant aluminous clay minerals are identified from orbit, but such compositions might occur at all of the original candidate sites and the added range in composition is useful for calibration in general.

To prepare a durable sulfate phase, we synthesized anhydrite, chosen for its relative thermal stability and lack of water of hydration. Most other sulfate minerals hydrate and can change hydration state readily. Arcanite, K_2SO_4 , is one of the few sulfates that is a stable non-hydrate and was also considered but potassium is not abundant on the martian surface and anhydrite is more representative of Ca-sulfates that *Curiosity* might encounter on Mars (e.g., Clark et al. 2005). For the basaltic component, we used a specimen from Totavi, NM, USA, that has been analyzed many times as an internal standard for X-ray fluorescence analyses at Los Alamos National Laboratory (LANL).

Figure 1a is a ternary diagram showing the as-mixed weight proportions of basalt, anhydrite, and processed clay minerals (heated to 1000 °C) in the ceramic targets. In describing the ceramics throughout this paper the terms “low S”, “mid S”, and “high S” are used as shown in this figure. Figure 1b shows discs of the ceramics after firing. The ceramic compositions and mixing proportions are detailed in Table 1. In concept, these targets mimic potential sediments or regolith on Mars that contain detrital basaltic sands along with either detrital or authigenic phyllosilicates and salts. As noted above, sedimentary mixtures of detrital basalt with reworked and reprecipitated sulfate minerals have been proposed for some of the best exposed sediments at the MER *Opportunity* site on Meridiani Planum (McLennan et al. 2005). Whether clay minerals are also present in those sediments is not known. However, observations from orbit suggest both clay minerals and sulfates occur interstratified, and potentially in intimate association, within the sedimentary sequence at Gale Crater (Milliken et al. 2010). The goal of ceramic target preparation was to represent the chemical makeup of such assemblages in a form durable enough to survive as analytical targets on *Curiosity*. Durability with the best possible homogeneity and finest possible grain size was desired. Meeting these goals required testing of possible preparation methods prior to target fabrication.

Fig. 1 (a) Ternary view of weight-percent ceramic target compositions for ChemCam based on sulfate, phyllosilicate, and basalt constituents expected to be common at Gale Crater. (b) Photographs of the four as-fired ceramic targets

1.2 Ceramic Synthesis Tests and Fabrication

The anhydrite used in fabricating ceramic targets was prepared from Mallinckrodt® reagent $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by stepwise heating to 800 °C over 6 h with a hold at 800 °C for 2.5 h. The product was confirmed by XRD to have an anhydrite structure. The anhydrite produced at this temperature was tested by exposure for a year at 100 % RH and room temperature; no rehydration was observed at these conditions. Reagent $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ heated at lower temperatures also produced anhydrite structures but could rehydrate at room conditions (e.g., ‘soluble anhydrite’ as described in Christensen et al. 2008). The higher-temperature anhydrite was used in order to minimize weight changes in the ceramics during fabrication; the anhydrite component of the ceramics has a similar heating and cooling profile and should be stable during flight and on Mars.

The basaltic component used in the ceramic targets was collected from exposures of a 2.3 Ma lava flow above Totavi, New Mexico, USA. The Totavi basalt is an olivine-phyric tholeiitic basalt that was collected, crushed, and powdered in large quantity for use as an internal standard in the Geology and Geochemistry X-ray fluorescence (XRF) Laboratory at LANL. Splits of this powder have been analyzed more than 200 times over the past 25 years; the average analysis is shown in Table 1. The composition of this powder is well constrained and the variability for all major elements between repeat analyses is within ± 2 % relative of the value listed.

The clay mineral components of the ceramics were reference samples obtained from the Clay Minerals Society. Emphasis was on Fe-rich clay minerals, which appear to be among the most common clay minerals on Mars. Australian nontronite NAu-2 from the Uley graphite mine in southern Australia was selected for this reason. Three of the ceramics were made with this nontronite (Fig. 1a, b). The fourth ceramic contains kaolinite KGa-2 from Warren County, Georgia, USA, to support analysis of martian samples containing a highly aluminous clay mineral. Note that these clay minerals are not completely pure but the minor contributions from other phases are evenly distributed. NAu-2 contains submicron

Table 1 Components used in syntheses

	Raw Clay NAu-2	1000 °C fired NAu-2	Raw Clay KGa-2	1000 °C fired KGa-2	Totavi basalt	Anhydrite	Li Tetra- borate
Analysis method	ICP	XRF	ICP	XRF	XRF	Reagent	Reagent
SiO ₂	48.70	55.50	44.50	52.65	50.66	—	—
Al ₂ O ₃	4.53	5.36	36.81	44.39	15.55	—	—
TiO ₂	0.595	0.724	2.182	2.496	1.42	—	—
Fe ₂ O ₃ (T)	31.76	33.42	0.82	0.92	11.54	—	—
MnO	0.016	0.02	0.00	0.01	0.16	—	—
MgO	0.77	0.88	0.04	0.05	7.30	—	—
CaO	1.96	2.39	0.02	0.09	8.82	41.19	—
Na ₂ O	0.70	0.78	0.02	0.04	3.14	—	—
K ₂ O	0.13	0.17	0.07	0.10	0.97	—	—
P ₂ O ₅	0.08	0.10	0.06	0.08	0.30	—	—
SO ₃	—	—	—	—	—	58.81	—
Li ₂ O	—	—	—	—	—	—	82.33
B ₂ O ₃	—	—	—	—	—	—	17.67
LOI	11.69	—	14.63	—	—	—	—
Total	100.93	99.35	99.15	100.80	99.86	100.00	100.00

Weight percentages used in ceramics						
	Dehydrated NAu-2	Dehydrated KGa-2	Totavi basalt	Anhydrite	Li Tetraborate	
NAu-2 low S	45.50		35.50	10.00	9.00	
NAu-2 mid S	45.50		22.75	22.75	9.00	
NAu-2 high S	45.50		10.00	35.50	9.00	
KGa-2 mid S		45.50	22.75	22.75	9.00	

Raw clay analyses are as-received from the Clay Minerals Society and include some mineral impurities in addition to the clay mineral (Fig. 5); 1000 °C fired clays represent the same material pre-fired (prior to ceramic formulation) to prevent hydration while processing ceramics. Compositions by ICP are from Actlabs; compositions by XRF were obtained at University of Massachusetts with the exception of the Totavi basalt, which is a LANL reference material. Reagent compositions (CaSO₄ as anhydrite and lithium tetraborate) are as-certified

carbonate and iron oxyhydroxide (Keeling et al. 2000) while KGa-2 has been reported to have 3 % anatase, 1 % crandallite, and traces of mica and/or illite (Chipera and Bish 2001). Our XRD analysis of the as-received NAu-2 sample shows presence of a trace amount of feldspar; anatase is present in the as-received KGa-2 (Fig. 2) but we did not detect crandallite or mica/illite.

Low-temperature preparation of grain mixtures in a binder was considered but faced problems because the most promising binders were organic compounds incompatible with MSL requirements; in addition, the ratio of binder to grains necessary for durability seemed excessive. Consideration was then given to firing the ceramics at a temperature low enough (≤ 800 °C) that sulfur in the sulfate mineral component would not be released. However, common clay-based ceramics are generally fired to much higher temperatures. “High-fire”

Fig. 2 X-ray diffraction analyses of as-received Clay Minerals Society source nontronite NAu-2 and kaolinite KGa-2, compared with analyses of the products obtained after pre-firing to 1000 °C. Phase symbols are F = feldspar, O = orthorhombic Fe_2O_3 ($\epsilon\text{-Fe}_2\text{O}_3$), and T = TiO_2 (anatase). All data were collected at the same conditions and variation in the scale of the vertical axis is sample-dependent

ceramics are fired to peak temperatures of ~ 1300 °C (“cone 10” to a potter), and even ceramics considered “low-fire” are fired to ~ 1000 °C (“cone 06” to a potter). Trials were performed with firing of both dry and slurry mixtures of several different Clay Minerals Society source clays, including ferruginous smectite SWa-1 from Grant County, Washington, USA, and sodium montmorillonite SWy-1 from Crook County, Wyoming, USA, as well as the nontronite NAu-2 and kaolinite KGa-2 ultimately used in making the ceramic targets. These source clays were mixed with powdered anhydrite and Totavi basalt in variable ratios and fired to 800 °C. However, all of the fired products were powdery, friable, and extremely weak. Examination showed that even after firing to 800 °C the clay mineral components retained the ability to expand and contract with changes in humidity, making the test samples unstable. At this point, it was decided to pre-fire the clay-mineral component at 1000 °C. This practice is used routinely at LANL (e.g., Vaniman et al. 2002) for analysis of clay minerals by XRF, in order to maintain accurate sample weights in fused-disc preparation. Heating at 1000 °C destroys the clay-minerals’ crystalline structure and thereby their ability to rehydrate. Pre-firing at this temperature does not result in significant loss of volatile components other than water and hydroxyl. The pre-fired kaolinite and nontronite lost all clay mineral structure and became mixtures of X-ray amorphous material plus either anatase in KGa-2 or $\epsilon\text{-Fe}_2\text{O}_3$ (orthorhombic Fe_2O_3) and feldspar in NAu-2 (Fig. 2).

With pre-fired clay minerals it was necessary to supplement the fired clay, basalt, and anhydrite mixtures with a flux to allow the mixture to sinter at 800 °C. A common potter’s method for promoting sintering or melting of clay bodies and glazes is to add a borate,

such as commercial “Gerstley Borate” obtained from mines near Death Valley, California, USA. Such commercial materials are complex mixtures (e.g., Gerstley Borate is a mixture of colemanite, ulexite, and hectorite plus minor contaminants). To maintain better control of our composition, we tested additions of chemically pure lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) that is used routinely in higher amounts (e.g., ~ 10 times sample powder) to make fused discs for XRF analysis of rock powders. Varying amounts of lithium tetraborate were mixed with powders of the Totavi basalt, anhydrite, and several pre-fired source clays (SWa-1, NAu-2, and KGa-2) and fired to 800 °C. Results of these tests indicated that in samples with a $\text{Li}_2\text{B}_4\text{O}_7$ content of 15 %, numerous microcracks appeared on cooling; samples with 20 % flux and higher were weakened by extensive glass formation. Vesiculation became more extensive as the addition of flux increased and at flux concentrations > 50 %, immiscible bodies of anhydrite up to ~ 2 mm in diameter formed. However, at flux concentrations between 5–10 % by weight, ceramics were formed of moderate grain size (< 100 μm) with minimal vesiculation (< 30 % vesicles of ~ 100 – 200 μm or less). The flux concentrations near 5 % produced softer ceramics, readily scratched by a steel probe, whereas flux concentrations near 9–10 % produced the hardest nontronite-based ceramics. Kaolinite-based ceramics were softer than the smectite-based ceramics. As a result of these tests, it was determined that all of the ceramic mixtures would be fired with 9 wt.% $\text{Li}_2\text{B}_4\text{O}_7$ flux.

The Totavi basalt powder, pre-fired nontronite, and pre-fired kaolinite were each ground in a W-carbide shatterbox before mixing with other components. The prepared anhydrite was hand-ground in an agate mortar before mixing. Lithium tetraborate that was added to the mixture was available as a finely-powdered product from SPEX[®] and required no pre-grinding before mixing. Each of the four ceramic formulations was prepared as a carefully-weighed 50 g single batch. All four-component mixtures (basalt, anhydrite, pre-fired clay mineral, and Li-tetraborate) were first mixed by hand and then ground in a W-carbide shatterbox twice, first for 45 min and then remixed by hand and re-ground in the shatterbox for another 20 min. Microscope analysis of grains in oil showed that the powders produced are mostly 5–15 μm , although rare (< 1 %) grains of basalt up to 75 μm remain.

The mixed powders for each ceramic were dry pressed at 7×10^3 kg for seven min to create cohesive samples for firing. A special die of sleeve, piston, and platens was machined from tool steel to produce pressed powders of the right diameter (23 mm) to fit the 22 ± 0.5 mm ChemCam standard holder on the *Curiosity* rover deck. The press piston diameter of 23 mm allowed for 3.8 % to 4.8 % shrinkage after firing (as determined from test samples), with greatest shrinkage in compositions of higher sulfur content. Initial attempts at pressing each disc individually to a thickness of ~ 4 – 5 mm to fit the ChemCam standard holder failed. At this thickness, the pressed powders had a persistent tendency to spall as soon as pressure was released. After multiple failures, it was found that spallation could be eliminated by pressing a larger sample, 11 to 13 mm thick, and cutting two discs of the required thickness from each of the taller cylinders after firing.

Weights of the pressed powder cylinders were ~ 10 g; the kaolinite cylinders were tallest in order to attain this weight. Each pressed cylinder was fired in the same manner, following the heating and cooling cycle shown in Fig. 3. To minimize loss of structural integrity, the pressed samples were heated in temperature increments of no more than 100 °C before being held at 800 °C for one hour. Firing and cooling were accomplished under ambient atmosphere and the samples were allowed to cool ballistically in the furnace; cooling times to < 100 °C were ~ 8 hrs. Weight losses on firing were ~ 0.4 % for all of the ceramics except the NAu-2 low S composition, which had a weight loss of ~ 0.3 %.

As noted above, shrinkage of the ceramics on firing varied with composition. All of the pressed-powder cylinders were 23 mm in diameter. Diameters of the ceramic products

Fig. 3 Oven temperature record of firing cycle for ChemCam ceramic targets. Note drying period of 14 hours at 90 °C before rise to 105 °C for an hour and ramp to 800 °C with one hour holds at 150, 200, 300, 400, 500, 600, 700, and 800 °C

ranged from 22.5 mm in the KGa-2 mid S composition to 22.0 mm (NAu-2 low S), 21.9 mm (NAu-2 mid S), and 21.6 mm (NAu-2 high S). Bulk densities of the ceramics are greatest in the NAu-2 compositions (2.27–2.42 g/cm³) and significantly lower in the KGa-2 ceramic (1.75 g/cm³), as expected based on the much lower density of kaolinite relative to nontronite. However, among the nontronite-based ceramics, density decreased as the ratio of basaltic powder to Ca-sulfate increased, despite the greater grain density of basalt. This is attributed to greater shrinkage and compaction with higher sulfur content.

After firing, discs of 4–5 mm thickness were cut from the 11–13 mm tall ceramic cylinders using a thin diamond blade in an Isomet[®] saw. High-purity ethanol was used as a cooling fluid (rather than water) during cutting. Remnants after cutting two 4–5 mm thick discs were used to make thin sections for optical and microbeam analysis. Some uncut cylinders were used for XRF and ICP/IR analysis. All powder collected during cutting was reserved and used for XRD analysis, although it was eventually found that some of the anhydrite in powder collected from the saw had hydrated to gypsum despite the use of ethanol in cutting. This is likely a result of ethanol hydration. For this reason, representative discs of the finished ceramics were eventually sacrificed for powder XRD analysis.

2 Analytical Methods

2.1 Powder X-Ray Diffraction (XRD)

Powder X-ray diffraction data were obtained with a Siemens D500 diffractometer using Cu K α radiation, incident- and diffracted-beam Soller slits, and a Kevex Si(Li) solid-state detector, measuring from 2° to 70° 2 θ . Powdered samples were analyzed in front-packed glass sample holders with cavities large enough to completely contain the X-ray beam. XRD analyses were obtained for the NAu-2 and KGa-2 bulk samples as received from the Clay Minerals Society, for the material obtained by pre-firing these at 1000 °C, for the Totavi basalt, and for all four of the ceramic compositions after firing. Diffraction patterns were analyzed with JADE[®] software from Materials Data Incorporated.

2.2 X-Ray Fluorescence (XRF)

The Totavi basalt XRF measurements given in Table 1 were made at LANL. All the other XRF data in Tables 1 and 2 were measured in the XRF lab at the University of Massachusetts using standard operating procedures (Rhodes 1996; Rhodes and Vollinger 2004). For the XRF analysis of major elements, samples were prepared as fused La-bearing lithium borate

glass discs using the methods of Norrish and Hutton (1969), though each sample was first ignited at 1040 °C for several hours in order to oxidize the iron to Fe^{3+} and remove volatiles. All elements (including Na) were measured simultaneously using a Siemens MRS-400 spectrometer. Estimates of accuracy and precision are given in Rhodes (1996) and $1-\sigma$ errors are presented in the footnote to Table 2. Sulfur was measured on a Panalytical 2400 sequential X-Ray spectrometer on a separate glass disc that was fused with an excess of lithium nitrate to ensure oxidation and retention of the sulfur as sulfate.

2.3 Instrumental Neutron Activation Analyses (INAA)

Some trace and minor elements (Table 3) were analyzed using INAA at Actlabs in Ancaster, Ontario. For that procedure, 1 g aliquots were analyzed along with internal standards at a thermal neutron flux of $7 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ and counted with a high-purity Ge detector. Results were calibrated against certified international reference materials. Several samples were reanalyzed to check the results. Detection limits are given in Table 3.

Chlorine was also analyzed by INAA following the same irradiation sequence noted above, after Al and other very short-life isotopes had decayed. The detection limit for Cl is 0.01 %; measured Cl in all samples was below this value except for sample KGa-2, which contained 0.03 % Cl.

2.4 Boron Analysis by Prompt Gamma Neutron Activation (PGNAA)

For PGNAA analysis of boron, 1 g samples in polyethylene vials were exposed at Actlabs to thermalized neutrons and the Doppler-broadened prompt gamma peak at 478 KeV was measured. Certified reference materials were used for calibration. Detection limits of the method are better than 1 ppm but the recommended upper limit for the method is ~ 1 %, somewhat lower than the 2.3 % boron expected in the ceramics. The PGNAA results for boron as borate are reported in Table 2 but are not used in representing the preferred composition because the reported values fall outside the recommended range of the method.

2.5 Infrared Analyses (IR)

For IR analysis of C and S at Actlabs, accelerator material was added to a 0.2 g sample to couple with the high frequency field of the induction furnace in a pure oxygen environment. During combustion, carbon-bearing components reacted to produce CO_2 and a lesser amount of CO. Sulfate reacted to form SO_2 and sulfur was measured as SO_2 in an IR cell. For this procedure, results are reported as “IR” in Table 2.

The small amount of CO was oxidized to CO_2 in a catalytic heater and total CO_2 was measured in an IR cell; energy from the IR source was absorbed as the gas passed through the cell and all other IR energy was prevented from reaching the IR detector by a narrow bandpass filter. Absorption of IR energy can thus be attributed only to CO_2 . An Eltra CS-2000 detector was used for the analysis. Detection limits for C and S in this process are 0.01 %. Measured C values for all samples were very close to this detection limit (0.04 % for shergottite, N Au-2 low S, N Au-2 high S, and N Au-2 mid-S; 0.06 % for KGa-2 mid-S and for raw clay sample of KGa-2; and 0.03 % for the raw clay sample of N Au-2) and therefore are not reported in Table 2.

Sulfur was also analyzed at Actlabs using the “Leco method,” which yields SO_2 analyses that are recalculated as SO_3 for tabulation (“Leco IR” in Table 2) with detection limits of 0.3 %. In this procedure a 0.2 g sample was combusted at 550 °C in pure oxygen. Sulfur-bearing components release S that is oxidized to SO_2 in the oxygen environment and measured as such in an infrared cell.

Table 2 Major- and minor-element analyses

Sample	Technique	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ ^a	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	LOI	Li ₂ O ^b	B ₂ O ₃	Total
NAu-2 low S #9	Predicted	43.41	0.840	7.99	19.38	0.07	3.00	8.37	1.48	0.42	0.15	5.94		1.60	7.44	100.09
	XRF (<i>n</i> = 3) ^c	44.11	0.75	7.75	20.27	0.076	2.92	8.34	1.47	0.41	0.14	6.51 ^c	0.22			
	XRF stdev	0.08	0.00	0.03	0.04	0.003	0.03	0.02	0.03	0.00	0.00	0.12				
	PGNAA														8.40	
	FUS-ICP ^d	43.46	0.80	7.51	20.37	0.07	3.01	8.18	1.42	0.40	0.14		0.36			
Average of (XRF)+(FUS-ICP) ^g	Leco IR											5.17				
	IR	43.78	0.78	7.63	20.32	0.07	2.97	8.26	1.44	0.40	0.14	5.33	0.22	1.60	7.44	100.39
	Predicted	36.92	0.650	6.00	17.90	0.05	2.07	12.51	1.07	0.30	0.11	13.43		1.60	7.44	100.05
	XRF (<i>n</i> = 3) ^c	37.66	0.56	5.75	18.93	0.054	2.01	12.23	1.13	0.28	0.11	12.74 ^c	0.18			
	XRF stdev	0.03	0.00	0.02	0.02	0.003	0.05	0.02	0.07	0.00	0.00	0.29				
NAu-2 mid S #20	PGNAA														8.34	
	FUS-ICP ^d	37.29	0.58	5.69	18.98	0.05	2.09	12.32	1.08	0.29	0.09		0.77			
	Leco IR											13.67				
	IR	37.48	0.57	5.72	18.95	0.05	2.05	12.27	1.11	0.29	0.10	13.54	0.18	1.60	7.44	101.34
	Average of (XRF)+(FUS-ICP) ^g	30.42	0.470	4.01	16.42	0.03	1.13	16.65	0.67	0.18	0.07	20.95		1.60	7.44	100.04
NAu-2 high S #11	Predicted	31.06	0.37	3.71	17.50	0.038	1.13	15.95	0.66	0.16	0.07	20.24 ^c	0.28			
	XRF (<i>n</i> = 3) ^c	0.08	0.01	0.03	0.06	0.002	0.04	0.05	0.05	0.00	0.00	0.03				
	XRF stdev															
	PGNAA														8.89	
	FUS-ICP ^d	30.73	0.403	3.68	17.52	0.03	1.16	16.6	0.68	0.17	0.06		1.03			
Average of (XRF)+(FUS-ICP) ^g	Leco IR											21.34				
	IR	30.90	0.39	3.69	17.51	0.03	1.14	16.28	0.67	0.16	0.06	21.07	0.28	1.60	7.44	101.22
	Predicted															
	XRF (<i>n</i> = 3) ^c															
	XRF stdev															

Table 2 (*Continued*)

Sample	Technique	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ ^a	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	LOI	Li ₂ O ^b	B ₂ O ₃	Total
KGa-2 mid S #14a	Predicted	35.37	1.450	23.66	3.03	0.04	1.68	11.38	0.73	0.26	0.10	13.34		1.60	7.44	100.08
	XRF (<i>n</i> = 3) ^c	35.98	1.44	24.05	3.15	0.053	1.66	11.50	0.71	0.26	0.11	12.26 ^c				
	XRF stdev	0.18	0.01	0.07	0.03	0.003	0.07	0.07	0.06	0.00	0.00	0.19				
	PGNAA														8.95	
Average of (XRF)+(FUS-ICP) ^g	FUS-ICP ^d	35.31	1.494	23.38	3.2	0.04	1.69	11.43	0.74	0.27	0.09		anom ^f			
	Leco IR											13.67				
	IR											13.13				
		35.64	1.47	23.71	3.18	0.05	1.68	11.46	0.72	0.26	0.10	13.40		1.60	7.44	100.71
Shergottite, glass #3	Fabre ^e	48.50	0.400	11.00	18.87		7.00	14.50	1.50	0.10						101.87
	XRF (<i>n</i> = 2) ^c	48.18	0.43	10.66	18.81	0.01	6.12	13.86	1.45	0.10	0.00	-0.03				
	PGNAA														0.00	
	FUS-ICP ^d	49.26	0.552	10.78	19.58	0.00	6.26	13.79	1.46	0.12	<0.01					
Average of (XRF)+(FUS-ICP)+(ICP-MS)+(EMPA) ^g	Leco IR											<0.3				
	ICP-MS ^e	48.43	0.400		19.17		6.15	14.34	1.53	0.12						
	EMPA ^e	48.41	0.450	10.83	19.59		6.62	14.15	1.61	0.10						
		48.57	0.46	10.76	19.29	0.01	6.29	14.03	1.51	0.11	0.00	0.00		0.00	0.00	101.03

Table 2 (Continued)

Sample	Technique	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ ^a	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	LOI	Li ₂ O ^b	B ₂ O ₃	Total
NAu-2 fired at 1000 °C	XRF (<i>n</i> = 3) ^c	55.50	0.724	5.36	33.42	0.022	0.88	2.39	0.78	0.17	0.10	0.00	0.70			100.05
	XRF stdev	0.13	0.02	0.01	0.06	0.001	0.01	0.01	0.02	0.00	0.00	0.12				
NAu-2 raw clay	PGNAA														0.00	
	FUS-ICP ^d	48.7	0.595	4.53	31.76	0.016	0.77	1.96	0.70	0.13	0.08		11.69			100.93
	Leco IR											<0.03				
	IR											0.21				
KGa-2 fired at 1000 °C	XRF (<i>n</i> = 2) ^c	52.65	2.50	44.39	0.92	0.01	0.05	0.09	0.04	0.10	0.08	0.00	−0.70			100.13
	PGNAA														0.00	
KGa-2 raw clay	FUS-ICP ^d	44.5	2.182	36.81	0.82	0.00	0.04	0.02	0.02	0.07	0.06		14.63			99.15
	Leco IR											<0.03				
	IR											0.12				

^aTotal Fe is reported as Fe₂O₃
^bLi₂O calculated based on stoichiometry of Li₂B₄O₇
^cThe number of replicate samples analyzed by XRF is listed as *n*. For the XRF data, 1- σ errors are 0.16 for SiO₂, 0.06 for Al₂O₃, 0.005 for TiO₂, 0.03 for total Fe₂O₃, 0.04 for MgO, 0.005 for MnO, 0.03 for CaO, 0.09 for Na₂O, 0.003 for P₂O₅, and 0.006 for K₂O in units of wt.% oxide. XRF data for SO₃ were not included in averages because they are not as precise as the IR values
^dDetection limits for fusion ICP are 0.01 % for all oxides listed and LOI (loss on ignition), except for TiO₂, which is 0.005 %. See www.actlabs.com
^eData from Fabre et al. (2011)
^fFUS-ICP LOI for KGa-2 mid S was anomalously high (7.85 wt.%)
^gComposition averages are shown as bold text for columns SiO₂ through SO₃; columns LOI through B₂O₃ are not averaged but show the preferred value
Note: Blank cells in this table indicate elements that were not analyzed by that technique

Table 3 Trace-element data for finished ceramics and raw clay samples

Analyte	Unit	D.L.	Method	NAu-2 low S	NAu-2 mid S	NAu-2 high S	KGa-2 mid S	NAu-2 raw	KGa-2 raw
Ag	ppm	0.5	ICP-MS	0.6	<0.5	<0.5	<0.5	<0.5	0.8
As	ppm	0.5	INAA	<0.5	<0.5	<0.5	2.9	<0.5	<0.5
As	ppm	5	ICP-MS	<5	<5	<5	<5	<5	<5
As	recommended			<0.5	<0.5	<0.5	2.9	<0.5	<0.5
Au	ppb	2	INAA	92	8	32	68	<2	<2
Ba	ppm	3	FUS-ICP	162	107	56	140	46	83
Be	ppm	1	FUS-ICP	<1	<1	<1	1	1	2
Bi	ppm	0.1	ICP-MS	<0.1	<0.1	<0.1	0.3	<0.1	0.7
Br	ppm	0.5	INAA	<0.5	<0.5	2.2	<0.5	<0.5	<0.5
Ce	ppm	0.05	ICP-MS	73.6	16.3	13.7	77.7	8.58	139
Co	ppm	1	ICP-MS	48	35	19	37	13	5
Cr	ppm	5	INAA	81	57	37	61	55	74
Cr	ppm	20	ICP-MS	120	80	50	90	40	40
Cr	recommended			81	57	37	61	55	74
Cs	ppm	0.1	ICP-MS	0.2	0.2	0.1	0.2	0.1	<0.1
Cu	ppm	10	ICP-MS	30	20	10	30	<10	<10
Dy	ppm	0.01	ICP-MS	2.81	1.68	1.22	3.43	0.95	4.34
Er	ppm	0.01	ICP-MS	1.61	0.93	0.68	1.74	0.54	2.02
Eu	ppm	0.005	ICP-MS	0.842	0.512	0.331	1.14	0.376	1.6
Ga	ppm	1	ICP-MS	10	7	5	40	4	56
Gd	ppm	0.01	ICP-MS	2.84	1.61	1.11	3.86	1.01	5.37
Ge	ppm	0.5	ICP-MS	0.7	<0.5	<0.5	2.2	<0.5	2.8
Hf	ppm	0.1	ICP-MS	1.5	1	0.7	4.3	1	5.8
Ho	ppm	0.01	ICP-MS	0.55	0.33	0.24	0.65	0.19	0.77
In	ppm	0.1	ICP-MS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ir	ppb	5	INAA	<5	<5	<5	<5	<5	<5
La	ppm	0.05	ICP-MS	47.8	8.93	6.45	46.3	4.46	83.9
Lu	ppm	0.002	ICP-MS	0.229	0.147	0.126	0.248	0.117	0.277
Mo	ppm	2	ICP-MS	<2	<2	<2	<2	<2	3
Nb	ppm	0.2	ICP-MS	39.1	12.7	15.6	35.1	5.9	49.8
Nd	ppm	0.05	ICP-MS	23.3	7.55	5.13	30	4.42	51.2
Ni	ppm	20	ICP-MS	70	60	50	40	50	20
Pb	ppm	5	ICP-MS	<5	<5	<5	34	<5	63
Pr	ppm	0.01	ICP-MS	7.55	2.01	1.41	9.48	1.09	15.9
Rb	ppm	1	ICP-MS	9	6	4	6	3	2
Sb	ppm	0.2	INAA	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Sb	ppm	0.2	ICP-MS	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Sb	recommended			<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Sc	ppm	0.1	INAA	9	7.2	5.5	9.7	14.8	16.8
Sc	ppm	1	FUS-ICP	16	13	10	15	15	17
Sc	recommended			9	7.2	5.5	9.7	14.8	16.8
Se	ppm	3	INAA	<3	<3	<3	<3	<3	<3

Table 3 (Continued)

Analyte	Unit	D.L.	Method	NAu-2 low S	NAu-2 mid S	NAu-2 high S	KGa-2 mid S	NAu-2 raw	KGa-2 raw
Sm	ppm	0.01	ICP-MS	3.38	1.68	1.14	5.06	1.09	7.82
Sn	ppm	1	ICP-MS	4	1	1	7	<1	12
Sr	ppm	2	FUS-ICP	236	185	144	152	134	59
Ta	ppm	0.01	ICP-MS	4.26	1.55	1.61	3.19	0.33	4.43
Tb	ppm	0.01	ICP-MS	0.47	0.28	0.2	0.63	0.16	0.82
Th	ppm	0.05	ICP-MS	1.55	0.82	0.53	9.49	0.34	16.2
Tl	ppm	0.05	ICP-MS	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Tm	ppm	0.005	ICP-MS	0.233	0.133	0.102	0.251	0.086	0.288
U	ppm	0.01	ICP-MS	0.77	0.38	0.33	3.68	0.28	5.9
V	ppm	5	FUS-ICP	129	105	81	78	131	64
W ^a	ppm	0.5	ICP-MS	545	360	209	360	2	9.1
Y	ppm	0.5	ICP-MS	15.9	9.4	7.1	17.6	4.9	17.3
Yb	ppm	0.01	ICP-MS	1.47	0.86	0.7	1.59	0.62	1.82
Zn	ppm	30	ICP-MS	90	70	60	50	130	<30

D.L. = detection limit

^aNote that powders for the ceramics were processed with W-carbide

2.6 Fusion Inductively-Coupled Plasma (FUS-ICP) and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)

For ICP analysis, samples were prepared and analyzed at Actlabs using methods described on their web site at www.actlabs.com. Each batch contained a reagent blank, certified reference materials, and 17 % replicates. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The melt was poured into 5 % nitric acid with an internal standard and stirred until dissolved. The samples were analyzed for major oxides and selected trace elements (FUS-ICP in Tables 2 and 3) using a Thermo Jarrell-Ash ENVIRO II ICP.

For ICP-MS analysis at Actlabs, reagent blanks with and without the lithium borate flux were analyzed, as well as the method blank. Interference correction verification standards were also analyzed. Calibration was performed using USGS and CANMET certified reference materials. The sample solution was spiked with internal standards and was further diluted and introduced into a Perkin Elmer SCIEX ELAN 6000 ICP/MS using a proprietary Actlabs method.

2.7 Microbeam Analysis of Ceramic Discs by Scanning Electron Microscopy (SEM)

In order to determine compositional and textural homogeneity, ceramic discs were also examined using a JEOL 5800LV Scanning Electron Microscope (SEM) operating at a low vacuum of 29 Pa, an accelerating voltage of 20 kV, and a beam current of 0.20 nA. Low vacuum was required because the ceramic rounds were placed directly in the vacuum chamber with no carbon coating or additional preparation; due to the limited availability of these calibration materials, the use of a conductive coating was avoided to preserve as much unmodified material as possible for potential future analyses with different techniques. Images were obtained using backscattered electrons (BSE) in order to highlight compositional variations associated with phases of differing average atomic weight.

2.8 Microbeam Analysis of Polished Thin Sections by Electron Microprobe

Thin-sections of the ceramics were analyzed for major and some trace element components using both wavelength-dispersive spectroscopy (WDS) and energy-dispersive spectroscopy (EDS) on a JEOL 8200 Electron Probe Microanalyzer (EPMA). An accelerating potential of 15 keV was used, with beam current of 20 nA and spot sizes of either 1 or 10 μm . Standards for WDS were provided by a C.M. Taylor Company standard mount. Doubly-polished thin sections were carbon-coated to reduce charging. One to two linescans across the ceramics were performed, totaling ~ 200 to 350 spot analyses. The beam was positioned to avoid obvious vesicles but a point spacing of $\sim 100 \mu\text{m}$ was maintained. Elements analyzed included B, Na, Mg, Al, Si, S, Ca, and Fe in linescans with 1 μm spot size for all of the ceramics. Additional linescans at 10 μm spot size included Ti in the element suite; these additional linescans were performed on the KGa-2 mid S and NAu-2 low S ceramics.

2.9 Optical Analysis

Standard doubly-polished thin sections of the ceramics, 30 μm thick, were examined with an Olympus BH-2 petrographic microscope. The sections were analyzed in both transmitted and reflected light. Point-counting (1,000 points on a 250 μm grid) was used to measure the volume percentage of vesicles in each ceramic. Vesicle sizes were measured with a calibrated reticle.

2.10 Laser-Induced Breakdown Spectroscopy (LIBS)

LIBS data were used to assess the heterogeneity of the ceramic standards. Spectra were collected at LANL using the ChemCam flight model. Data were collected in a thermal vacuum chamber with the laser at -10°C , producing a maximum laser energy output of $\sim 15 \text{ mJ/pulse}$. Eighteen geochemical standards plus the 10 calibration targets were analyzed at 1.6 m stand-off distance. The LIBS spot size ($\sim 400 \mu\text{m}$) exceeded the largest grain size in the ceramics ($\sim 100 \mu\text{m}$). During analysis the chamber was held at 7 Torr CO_2 . Data were taken at 3 Hz, for a total of 50 shots at each of 4 analysis locations per target. Additional details on the ChemCam flight instrument and calibrations are presented in Wiens et al. ([this issue](#)). Spectra were normalized to the total emission intensity for each spectrograph and the first five spectra at each spot were discarded to discount any surface contamination.

3 Analytical Results and Characterization of the Ceramic Targets

3.1 Physical and Optical Properties

The ceramic targets based on nontronite NAu-2 are brick red with Munsell colors of 7.5YR2/4 (NAu-2 low S), 5YR2/4 (NAu-2 mid S), and 5YR1/2 (NAu-2 high S). The target based on kaolinite KGa-2 is somewhat mottled but overall very light brown in color (2.5Y4/4). Visible and near-infrared spectra of the ceramic targets are given in Wiens et al. ([this issue](#)). All of the ceramic targets are durable and retain the cylinder walls originally present in the pressed powders; they are readily cut with a diamond saw blade. As observed in prototype development, ceramics based on NAu-2 are harder than a steel probe but can be scratched with a sharp tungsten carbide probe. The ceramic based on KGa-2 is softer and can be scratched with a steel probe.

Fig. 4 Reflected-light photomicrographs of 30 μm thick doubly-polished thin sections of ChemCam ceramic targets. *Dark spots* are epoxy-filled vesicles; *bright grains* in the NAu-2 samples are hematite

Standard doubly-polished petrographic sections of the NAu-2 ceramics are opaque in plane-polarized transmitted light. In reflected light, the polished sections of these ceramics are vesicular with selvages of vitrification surrounding most vesicles (Fig. 4). Vesicle linings are not coated by any vapor-phase crystals but do entrain small grains of a few μm . In the ceramics based on NAu-2, vesicle abundance ranges from $\sim 20\%$ in the ceramic of lowest sulfur content to $\sim 30\%$ for the highest sulfur content. In the KGa-2 mid-S ceramic, vesicle abundance is $\sim 20\%$. Vesicle sizes are generally $< 100\ \mu\text{m}$, although a few of the vesicles in the KGa-2 mid-S ceramic range up to 200–300 μm . In both the NAu-2 and KGa-2 ceramics, fine grain size ($< 30\ \mu\text{m}$) is observed in zones surrounding vesicles; grains of $\sim 30\ \mu\text{m}$ are typical elsewhere but coarser grains (up to 100 μm) occur in areas not adjacent to vesicles. Commonly the coarsest grains in the NAu-2 ceramics are of anhedral hematite that may be up to 100 μm in diameter.

The petrographic section of the KGa-2 ceramic has a more complex fabric than the NAu-2 ceramics. Subangular bodies of very fine-grained matrix up to 2 mm in size are distributed in a coarser matrix (Fig. 4d). Because all of the pressed powders were sintered while free-standing and all maintained cylindrical form without distortion or flowing, these bodies are unlikely to be chilled rim portions that migrated into the body of the ceramic. Rather, the bodies of finer grain size are believed to represent heterogeneity in heating and cooling within the KGa-2 pressed powder cylinders.

3.2 Bulk Chemical Composition

Compiled major- and minor-element chemical analyses of materials used to produce the ceramics are listed in Table 1; analyses of the finished ceramics are listed in Tables 2 and 3. The bulk chemical compositions of the four ceramics match the predicted compositions within 5 % relative for all oxides present at >1 %. The conservation of weight on firing and retention of S abundance within 1 % of the pre-firing abundances within the mixed powder (except in the N Au-1 low S ceramic, which is within ~10 %) indicate that volatile element loss on firing was minimal. Each ceramic target has an average composition listed in bold text in Table 2, based on the average of XRF and FUS-ICP analyses, that is close to the planned, predicted value. Boron analyses however are problematic. The Actlabs PGNAA B₂O₃ measurements range from 8.34 to 8.95 wt.%, whereas expected B₂O₃ content of the ceramics is 7.44 wt.%. This discrepancy may arise because the boron content in the ceramics is about twice the recommended upper limit of the PGNAA method (see Sect. 2.4). For comparison, the multi-point microprobe averages for B₂O₃ vary from 5.8 to 7.4 wt.%, but for reasons discussed in Sect. 3.4 we find that low microprobe totals are common and the measured averages are generally lower than actual bulk concentration. The only usable direct measurement of B is that of the PGNAA, so that is reported in Table 2, although we do not use the PGNAA boron data in presenting the preferred value for the ceramics because of the method limitations. For the purposes of Table 2 we recognize the limitations on analysis for both Li and B and use the as-weighed lithium tetraborate powder abundance, used in preparing the ceramics, for the preferred composition.

3.3 X-Ray Diffraction

Powder X-ray diffraction patterns of the four ceramics are compared in Fig. 5 and estimates of weight abundance based on full-pattern fitting are tabulated in Table 4. All of the ceramics developed a significant amount of X-ray amorphous “glassy” binding material that is manifested as a broad, asymmetric rise in the diffraction background that peaks at ~24° 2-theta (Cu K α). This X-ray amorphous component includes borosilicate(s) and its abundance cannot be estimated by full-pattern fitting. However, the conservation of sulfur on firing (see discussion of chemical analyses), microprobe data indicating that S is correlated with Ca (i.e., present as crystalline CaSO₄), and the relative constancy of weight before and after firing allow the abundance of anhydrite to be used to adjust the relative proportions of crystalline and X-ray amorphous material accordingly. The results as presented in Table 4 are semi-quantitative.

All of the ceramics based on nontronite N Au-2 contain anhydrite, hematite, cristobalite, and remnant grains of plagioclase and augite from the powdered basalt. In the N Au-2 ceramic with the lowest sulfate content, remnant grains of plagioclase and augite are most abundant. Complex phases including silicates that incorporate Li and/or B from the flux are likely present as well; of these, virgilite (a lithium-aluminum silicate, LiAl₂Si₂O₆) occurs in all of the nontronite-based N Au ceramics. There is a bit of serendipity in the formation of virgilite within these ceramics, for the virgilite type locality is Macusani, Peru (French et al. 1978), where it was discovered within Macusani volcanic glass that happens to be used as the sole natural volcanic glass calibration target on ChemCam (Fabre et al. 2011). Virgilite also occurs synthetically in other lithium aluminum silicate glass-ceramics that are sintered at low temperature (e.g., Serbena et al. 2011).

The ceramic based on kaolinite KGa-2 contains anhydrite with remnant grains of plagioclase and augite from the powdered basalt. Virgilite may be present, but in trace amounts

Fig. 5 Powder X-ray diffraction patterns of the four ChemCam ceramics. Mineral symbols are A = anhydrite, C = cristobalite, F = feldspar, H = hematite, P = pyroxene (augite), V = virgilite. All data were collected at the same conditions and variation in the scale of the vertical axis is sample-dependent

difficult to confirm by XRD. The amorphous diffraction background is higher in the KGa-2 mid S ceramic than in any of the nontronite-based NAu-2 ceramics and glass linings of vesicles are more prominent in the KGa-2 ceramic than in the NAu-2 ceramics. The glassy component of the KGa-2 ceramic may contain most of the Li (and likely B) contributed from flux, accounting for the apparent absence of virgilite.

As noted in Sect. 1.2, the discs were synthesized with anhydrite but preliminary XRD analyses of “sawdust” collected during cutting of discs from the ceramic cylinders identified gypsum as well as anhydrite. However, as data accumulated from LIBS analysis of the ceramics it was noted that hydrogen detections were absent or very low and not in line with the occurrence of gypsum in any significant abundance. Because of this discrepancy, representative discs from each of the ceramics were sacrificed to be crushed for XRD analysis; none of these samples contained gypsum. It is apparent that even though the cylinders were cut with ethanol some hydration of anhydrite did occur, likely caused by hydration of the ethanol, to form gypsum in the fines collected from the saw. The XRD data summarized in Table 4 report the more accurate analyses obtained from crushed discs.

3.4 Electron Microbeam Results

Table 5 shows the average, standard deviation, minimum, and maximum values for Si, Al, Ca, Fe, Mg, Na, S, and B, recalculated as oxide weight percent, as analyzed by electron

Table 4 Phase detection and abundances (wt.%) determined by XRD in the ChemCam ceramic targets

	NAu-2 low S	NAu-2 mid S	NAu-2 high S	KGa-2 mid S
Plagioclase	7	2	tr ^a	4
Augite	6	3	tr	2
Cristobalite	4	5	5	–
Hematite	10	9	9	–
Virgilite	16	16	16	–
Anhydrite	10	23	36	23
Amorphous	47	42	33	71

^atr = trace (<1 %)**Table 5** Summary statistics for electron microprobe data

	SiO ₂	Al ₂ O ₃	CaO	FeO	MgO	Na ₂ O	SO ₃	B ₂ O ₃
NAu-2 low S								
average	42.7	7.8	7.5	17.1	3.8	1.7	4.5	7.4
st. dev.	6.5	4.6	3.1	6.8	5.5	0.9	2.3	4.8
max	55.7	24.2	18.9	38.0	31.0	4.9	11.6	23.0
min	12.1	0.0	0.2	2.1	0.2	0.0	0.0	0.0
NAu-2 mid S								
average	40.7	6.1	10.5	16.5	1.8	1.2	11.1	5.9
st. dev.	8.1	4.4	4.3	6.5	2.9	0.8	6.1	3.4
max	67.5	28.0	26.1	32.4	34.4	5.3	36.5	16.6
min	20.8	0.7	1.5	0.4	0.0	0.1	0.0	0.0
NAu-2 high S								
average	34.9	4.1	14.2	15.5	1.1	0.8	18.0	5.8
st. dev.	10.9	4.2	6.4	6.5	2.1	0.8	9.3	3.2
max	84.2	32.1	31.2	32.5	27.5	6.7	43.8	19.5
min	8.2	0.2	0.7	0.4	0.0	0.1	0.0	0.0
KGa-2 mid S								
average	32.4	21.8	9.1	2.1	1.5	0.8	10.4	6.0
st. dev.	7.4	5.9	3.5	3.5	4.6	0.6	5.0	7.4
max	67.7	37.7	20.2	29.0	42.3	3.9	20.9	29.8
min	19.3	0.0	0.1	0.5	0.0	0.0	0.0	0.0

Only analysis points with totals of 90–100 % are tabulated. This includes 194 analyses for NAu-2 low S, 183 for NAu-2 mid S, 191 for NAu-2 High S, and 215 for KGa-2 mid S

microprobe (Ti data are not tabulated as they were only obtained from a subset of the analytical points). Approximately 200 analysis points are represented for each of the ceramics and only points with totals between 90–100 % are tabulated. The causes of low analytical totals are discussed in more detail below.

Most of the points analyzed by electron microprobe contained both Si and S or Si and B, which do not occur together in any crystalline phase identified by XRD in the ceramics. This indicates that most analysis spots were mixtures of several minerals or glass within the

diameter of the microprobe beam (either 1 or 10 μm). Nevertheless, several of the points analyzed at these spot sizes were of individual grains of plagioclase, augite, olivine, and (rarely) ilmenite that represent nonmelted minerals of the Totavi basalt. These individual crystalline relics from the basalt, coarse enough to contain most of the 1–10 μm microprobe beam, comprise <2 % of the points analyzed. Individual grains of hematite in the NAu-2 ceramics, produced from orthorhombic Fe_2O_3 (Fig. 2) on firing of the ceramics, were avoided.

Statistical analysis of the microprobe data shows little correlation between any of the elements except Ca and S, as expected for samples containing anhydrite. The Ca–S correlation is strongest in the high-S NAu-2 ceramic ($R^2 = 0.97$), less in the mid-S NAu-2 ceramic ($R^2 = 0.92$), and very poor in the low-S ceramic ($R^2 = 0.28$). Poor correlation in the low S composition is attributable to the relative increase in volumetric proportion of Ca-bearing augite and plagioclase from the Totavi basalt. In the KGa-2 mid-S ceramic, the Ca–S correlation is also modest ($R^2 = 0.73$) and poorer than the correlation between Mg and Fe ($R^2 = 0.87$). The association of Fe with Mg in the KGa-2 ceramic arises because Fe is not segregated from Mg to form hematite as in the NAu-2 ceramics; in the KGa-2 ceramic these two elements are associated in remnant augite and (to lesser extent) olivine of the Totavi basalt powder. It is notable that the highest SO_3 content observed in any of the microprobe analytical points in all of the ceramics was 44 wt.%, far less than the 58.8 wt.% SO_3 of stoichiometric anhydrite. This indicates that none of the anhydrite in any of the ceramics was coarse enough to contain the electron microprobe beam.

Despite caution taken to avoid visible vesicles, many of the microprobe analysis points have low totals (<90 wt.% and as low as 70 wt.%). In part this is because of the presence of unanalyzed lithium at an abundance of 1.6 wt.% Li_2O in the bulk composition of all of the ceramics and possibly concentrated locally in either a glass phase or, in the NAu-2 ceramics, in the mineral virgilite (~ 4 wt.% Li_2O). In addition, Fe is reported as FeO but includes some fraction of ferric iron. Titanium was also not a part of the analysis suite in all microprobe analyses but where analyzed the abundance is low (KGa-2 mid S averages 1.4 wt.% TiO_2 and NAu-2 low S averages 0.4 wt.%). The lowest totals are in large part a result of micro-porosity. Totals below 90 wt.% are particularly common in the KGa-2 ceramic (55 % of all analysis spots) and the NAu-2 low S ceramic (43 %), but rare in the NAu-2 mid S ceramic (7 %) and the NAu-2 high S ceramic (5 %). The greater success of microprobe analysis of the higher-sulfur nontronite-based ceramics may have several causes but is believed to be principally associated with better matrix fusion (less microvesicularity) and with integration of anhydrite, virgilite, and a glass phase into a fine-grained and relative homogeneous glass ceramic. Unfortunately, the great variability in microprobe analytical totals limits the use of microprobe data in evaluating homogeneity of the ceramics.

Figure 6 compares ceramic target backscattered electron (BSE) surface textures of representative discs of the four ceramics. The brightest grains in BSE images of the NAu-2 samples are mostly hematite. All samples have vesicles ~ 10 – 100 μm in diameter, but a few larger vesicles (to 300 μm) occur in the KGa-2 mid S ceramic. All three NAu-2 samples have a consistent surface texture at the 50 μm scale, while the KGa-2 surface texture is more varied. By visual inspection prior to SEM analysis, the NAu-2 low S ceramic showed some evidence for smoother and rougher surfaces throughout the disc. However, at $100\times$ magnification there is no evidence for textural differences within the disc. Similarly, although in visual inspection the three NAu-2 ceramics appear to have increasing amounts of very faint ‘mottling’ in color from low S (not mottled) to high S (more mottled; Fig. 1b), these differences were not observed in BSE and do not appear to correlate with any compositional heterogeneity across the discs.

Fig. 6 Scanning Electron Microscopy (SEM) backscattered electron (BSE) images of ceramic calibration target surfaces at $100\times$ magnification. Scale bars in each image (black lines) are $500\ \mu\text{m}$. There are numerous rounded, shallow vesicles in all samples. Bright grains of $\sim 30\ \mu\text{m}$ can be seen in all samples, in particular the NAu-2 suite, where most of these grains are hematite

3.5 Laser-Induced Breakdown Spectroscopy (LIBS) Assessment of Composition and Heterogeneity

Examples of LIBS spectra for each ceramic are shown in Fig. 7. The ceramic targets were assessed for heterogeneity in several ways. These included visual inspection of the spectra and examination of line intensity variations between four different spots within each ceramic. Specific line intensity variations between the ceramic compositions were compared to other samples of reference composition. The other samples include a picrite glass that is one of the ChemCam glass calibration standards (Fabre et al. 2011) on *Curiosity*, a sample of the sulfate mineral melanterite (MHC2319), and several geostandards with accepted, recommended compositions (andesite AGV-2, andesite JA-2, basalt BIR-1, stream sediment STSD-1, and shale SGR-1). Statistical analysis included evaluation of variance in peak intensities between the four analyzed spots within each sample.

Visual inspection of all 200 spectra for each ceramic (50 spectra for each of four spots) was conducted. This inspection revealed no obvious differences in the form of missing or new major peaks. Second, for each sample the intensity at every wavelength channel was examined to determine if it was within the 99 % confidence level based on the standard deviation of the average intensity for the four analysis spots. Two spots were found to be significantly different: a spot in NAu-2 high S that is relatively low in Li and Ca and high in

Fig. 7 Example LIBS spectra of each ceramic; NAu-2 high S (green), NAu-2 mid S (black), NAu-2 low S (red), and KGa-2 mid S (blue). Plots are divided into three spectral ranges: 240–340 nm (top), 380–470 nm (middle), and 490–860 nm (bottom). Each spectrum is the average of 180 single shot spectra across 4 analysis locations; spectra have been normalized to the total emission, multiplied by 1000 and then offset by 5 units for clarity

Ti and Ba, and a spot in NAu-2 mid S that is relatively low in Li, Ca, Fe, Na and O. Figure 8 shows bivariate plots of Na vs. Mg and Li vs. Ca for all four analyses in each sample, with standard analytical errors. The plot of Na vs. Mg is typical of most bivariate plots in that the range of LIBS peak intensity variation in all four ceramics is comparable to the range for most other samples, including the geostandard powders. However, the plot of Li vs. Ca shows distinct outliers of lower intensity in both elements for NAu-2 mid S and NAu-2 high S, as well as a broad range of variation in the KGa-2 mid S ceramic. Outliers such as these have been observed in some powdered geostandards as well. Because the outlier in NAu-2 mid S is marked by decrease in peak intensity of most major elements in the ceramic, the cause of variation appears to be a drop in total LIBS intensity for all elements at that spot rather than compositional variation within the ceramic.

Notably absent in the statistical analysis of LIBS results for the four ceramics is a significant role for any of the sulfur emission lines, despite the great range of sulfur composition. This is discussed further below.

Fig. 8 Bivariate plots of LIBS emission line intensities for lines at 589 nm (neutral Na) vs. 279.6 nm (singly-ionized Mg) (*upper plot*) and 671 nm (singly-ionized Li) vs. 393.5 nm (singly-ionized Ca) (*lower plot*), with analytical error bars representing standard deviation of 45 LIBS shots within each spot (50 shots, with the first 5 discarded to account for any surface effects). For all samples, four different spots were analyzed. Fields for the four ceramics are shown, including error bars, except for two outliers (NAu-2 mid S and NAu-2 high S) in the 671 nm vs. 393.5 nm plot where emission line intensities for both Li and Ca lines are diminished. The samples shown for comparison include the ChemCam standard picrite glass (Fabre et al. 2011), an Fe-sulfate mineral (melanterite MHC2319), several powdered geostandards (andesite AGV-2, andesite JA-2, basalt BIR-1), a quartz-feldspar-amphibole-chlorite-mica stream sediment (STSD-1), and Green River shale (SGR-1)

4 Application of S-Bearing Granular Ceramics as ChemCam Calibration Targets on Mars

Granular ceramic targets are secondary to homogeneous glasses for chemical calibration of LIBS on Mars. Ceramics do however fill a unique role in calibration, particularly in representing a fine-grained mineral and glass mixture (Table 4), in their component of clay-mineral chemistry, and in their range of sulfur content present as sulfate. The chemical data compiled in Tables 2 and 3 provide an accurate summary of the bulk compositions of the ceramics. For comparative purposes, the chemical analyses of the shergottite glass obtained for this study are in excellent agreement with those from Fabre et al. (2011), indicating that analyses in Tables 2 and 3 of this paper can be compared along with the glass target compositions from that study.

Compared to the homogeneous glass calibration targets, ceramic targets are more heterogeneous on a fine scale, with vitrified, granular, and vesicular features ranging in size up to $\sim 100\ \mu\text{m}$. The target based on kaolinite, KGa-2 mid S, is more texturally heterogeneous, with glass-lined vesicles up to $300\ \mu\text{m}$ and fine-grained enclaves up to $\sim 2\ \text{mm}$. However, LIBS analyses of the ceramics (Fig. 8) suggest that compared to the KGa-2 ceramic there is either (1) more compositional variation, or (2) spot variation in total LIBS emission, in the mid-S and high-S ceramics based on nontronite (NAu-2).

Analysis of the LIBS spectra for the ceramics shows that, as reported by Sallé et al. (2004) and Dyar et al. (2011), direct detection of sulfur is difficult in LIBS analyses in a martian environment. The latter paper points out that transition probabilities for even the strong S lines are significantly smaller (at least an order of magnitude) than those for other “major” elements, so that S lines may be difficult to detect by routine methods, even in high-S samples. Although the NAu-2 high S composition contains 25 % SO_3 (10 % S) by weight, the S emission lines in LIBS at 545.5 and 564.7 nm are not well-resolved due to interference from the much stronger Fe emission in these compositions (this is not an issue in the KGa-2 mid S ceramic). Dudragne et al. (1998) suggest that the presence of sulfur induces chemical matrix effects in the remainder of the spectrum, potentially allowing a partial least squares (PLS) algorithm to determine the presence of S even in the absence of its emission lines. Dyar et al. (2011) did not obtain good results in S analysis using the entire LIBS spectrum, but showed that isolating specific subsets of the LIBS wavelength ranges near the S emission line locations allowed determination of non-zero correlation coefficients for PLS; this strategy was particularly successful for sulfate minerals. Quantification of sulfur using ChemCam data will be addressed in a forthcoming calibration paper because it presents challenges to routine PLS analyses and requires special procedures to get optimal results. These will be needed to mitigate effects from the Fe interference in ChemCam operations at Gale Crater, where sulfate phases are important components of sedimentary deposits that may also contain significant amounts of Fe-rich nontronite and basaltic detritus. However, comparative analytical results using APXS and potentially also CheMin and SAM at Gale Crater will refine the analytical methods for all elements. In addition, ‘round-robin’ blind samples and shared standards will be analyzed using flight-equivalent equipment for ChemCam, APXS, CheMin, and SAM; this should ensure proper characterization of samples at the Gale Crater site.

It is evident from the properties of the ceramics that heterogeneity of chemical composition is greater in the ceramic targets than in the homogeneous glasses (Fabre et al. 2011) that are carried in the ChemCam standard holder on *Curiosity*. However, the ceramics fill a unique role by adding potential calibration for S-bearing compositions. Many of the sediment and soil samples that will be encountered by *Curiosity* may contain the three major

geochemical components present in the ceramic targets: basaltic detritus, phyllosilicates (albeit in altered phase form within the ceramics), and sulfate. The ChemCam ceramics provide realistic targets for evaluating LIBS analysis of fine-grained S-rich samples on Mars.

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