

**INVESTIGATION OF MINERAL PHASE EFFECTS CAUSED BY SULFUR BEARING MINERALS IN A CUMBERLAND SIMULANT, USING LABORATORY EQUIVALENTS OF SAM, APXS, AND CHEMIN MARS SCIENCE LABORATORY INSTRUMENTS.** C. A. Knudson<sup>1,2</sup>, G. M. Perrett<sup>3</sup>, A. C. McAdam<sup>2</sup>, J. L. Campbell<sup>4</sup>, E. L. Flannigan<sup>4</sup>, R. V. Morris<sup>5</sup>, S. C. Andrejkovičová<sup>1,2</sup>, S. A. Mertzman<sup>6</sup>, S. W. Squyres<sup>6</sup>, P. R. Mahaffy<sup>2</sup>. <sup>1</sup>CRESST/UMCP, Center for Research and Exploration in Space Sciences and Technology/University of Maryland, College Park, MD, 20742, USA. (christine.a.knudson@nasa.gov). <sup>2</sup>NASA Goddard Space Flight Center, Greenbelt, MD, 20771, USA. <sup>3</sup>Department of Physics and Computer Science, Wilfrid Laurier University, Waterloo, ON, Canada. (gperrett@wlu.ca). <sup>4</sup>Guelph-Waterloo Physics Institute, University of Guelph, Guelph, ON, Canada. <sup>5</sup>NASA Johnson Space Center, Houston, TX, 77058, USA. <sup>6</sup>Franklin and Marshall College, Lancaster, PA, 17604, USA. <sup>7</sup>Cornell University, Ithaca, NY, 14850, USA.

**Introduction:** The Mars Science Laboratory (MSL) Curiosity rover carries a suite of instruments which provide complementary geochemical and mineralogical data to investigate the possibility of habitable conditions throughout martian history [1]. Here, we investigate a possible source for some of the observed differences in the measured quantities of sulfur, reported as  $\text{SO}_3$ , by the Sample Analysis at Mars (SAM) and Alpha-Particle X-Ray Spectrometer (APXS) [2] instruments (Figure 1), namely mineral phase effects (MPEs) in the APXS analyses [3]. Mixtures of different minerals ranging from simple two-phase mixtures to a multi-phase martian simulant, were created and analyzed to investigate the influence of a particular host mineral on APXS sulfur concentrations.

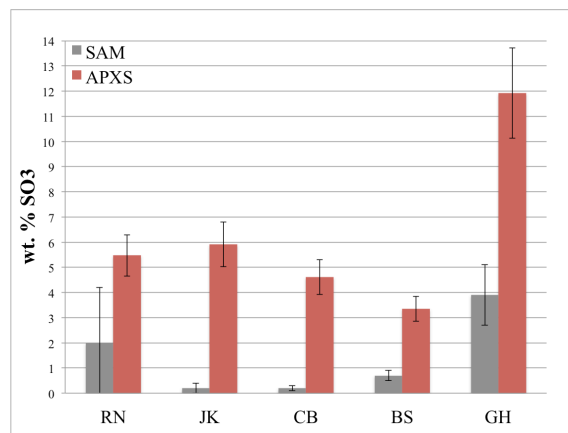


Figure 1.  $\text{SO}_3$  derived from SAM  $\text{SO}_2$  measurements (gray) compared to  $\text{SO}_3$  derived from APXS measurements (red) for selected samples analyzed by MSL (after Figure 12b in [2]). RN: Rocknest aeolian bedform material [e.g., 4]; JK: John Klein Sheepbed mudstone sample [e.g., 1]; CB: Cumberland Sheepbed mudstone sample [e.g., 1]; BS: Big Sky Stimson sandstone sample [e.g., 5]; GH: Greenhorn altered Stimson sandstone sample [e.g., 5].  $\text{SO}_3$  differences may result in part from MPEs in APXS analyses.

**Methods:** The Cumberland Simulant (CBS) is a simulant of the Cumberland (CB) drill sample of the Sheepbed mudstone analyzed in Gale Crater by SAM, APXS, and the Chemistry and Mineralogy Instrument (CheMin) between sols 282-408 [e.g., 1,6]. The simulant was created using the minerals and mineral abundances as determined by CheMin [7]. However, some minor mineral phases were substituted or combined (e.g. anhydrite was used in place of the minor amount of bassanite and augite was used for the two identified clinopyroxene phases, augite and pigeonite). All mineral phases were crushed and sieved to  $<63 \mu\text{m}$ . The individual minerals were first characterized by X-ray diffraction (XRD) and SAM-like evolved gas analysis (EGA) mass spectrometry at NASA Goddard Space Flight Center (GSFC) in Greenbelt, MD. Major element analyses on 19 individual phases were done by X-ray fluorescence (XRF) at Franklin and Marshall College in Lancaster, PA [8].

A total of 19 S-bearing mixtures were created to analyze the MPEs caused by the presence of a S-containing mineral alongside non-S-containing minerals. The minerals in these mixtures were in the same proportions as the CB sample, as well as in the full CB simulant (CBS) itself (Table 1). The simulant and each mineral mixture were mixed by mortar and pestle for three minutes [9]. The mixtures were then analyzed using laboratory equivalents of MSL instruments.

**APXS-like analyses.** The samples were pressed into pellets for XRF analyses at NASA GSFC on a Bruker M4 Tornado (Rh  $K\alpha$  radiation). The M4 Tornado has a 1 mm beam diameter; four spots were analyzed per sample (at 50 kV and 200  $\mu\text{A}$  for 10 minutes each). Pellets were pressed and carbon coated for analysis by Particle-Induced X-ray Emission (PIXE) (2.5 MeV protons) at the University of Guelph, Guelph, Ontario, Canada. PIXE has a 4x4 mm beam size which is comparable to the four 1 mm XRF spots. Measurement duration was 15 minutes. These two excitation methods approximate the analysis of martian targets by the MSL APXS instrument [3].

Mixture Name	Minerals/Phases in Mixture
PA	Pyrrhotite, Augite
PAF	Pyrrhotite, Augite, Forsterite
PAFE	Pyrrhotite, Augite, Forsterite, Enstatite
PALFE	Pyrrhotite, Augite, Labradorite, Forsterite, Enstatite
PM	Pyrrhotite, Magnetite
PGAF	Pyrrhotite, Griffith Saponite, Augite, Forsterite
PG	Pyrrhotite, Griffith Saponite
PH	Pyrrhotite, Hematite
PBas	Pyrrhotite, Basaltic Glass (PN708)
PPal	Pyrrhotite, Palagonite (HMWK101)
AnA	Anhydrite, Augite
AnAE	Anhydrite, Augite, Enstatite
AnAEL	Anhydrite, Augite, Enstatite, Labradorite
AnM	Anhydrite, Magnetite
AnG	Anhydrite, Griffith Saponite
AnH	Anhydrite, Hematite
CumbS	Cumberland Simulant (w/o Cl bearing phases)
Pal	Palagonite (HWMK101)
Bas	Basaltic Glass (PN708)

Table 1. Set of 19 Cumberland Simulant Mineral Mixtures used in this study.

**SAM-like EGA.** The CBS mineral mixture, and other mineral mixtures from Table 1, will be analyzed at NASA GSFC on a Setaram Labsys Evo Thermogravimeter/Differential Scanning Calorimeter coupled to a Pfeiffer OmniStar quadrupole mass spectrometer set up to operate under SAM-like heating and carrier gas flow conditions (~1 mL/min He flow rate and ~25 mbar of He gas pressure in the pyrolysis oven). The <63  $\mu\text{m}$  size fraction of the mixtures will be heated at a SAM-like ramp rate modeled after the CB sample temperature ramp rate to 850 °C. The amount of  $\text{SO}_2$  evolved from each mixture, as well as the complete simulant, will be compared to the CB sample analyzed by SAM on Curiosity [10,11]. These quantities will then be converted to equivalent  $\text{SO}_3$  values and compared to the  $\text{SO}_3$  quantities measured with the APXS-like analyses.

**CheMin-like analyses.** A portion of each mixture will be analyzed on the CheMin-4 XRD at NASA Johnson Space Center. Like the MSL instrument, the CheMin-4 employs transmission XRD geometry and a Co radiation source. These analyses will be used for comparison to the CB sample analyzed by the CheMin instrument onboard MSL in 2012.

**Results:** Figure 2 shows preliminary uncorrected PIXE results for selected mixtures in which S was detected compared to S concentrations calculated from XRF analyses of individual mineral glasses. Corrections of PIXE data are still ongoing, but we hypothesize that when this data is ultimately used to take MPEs into account, the  $\text{SO}_3$  concentrations reported by APXS will move closer to those reported by SAM. It should be noted however, that MPEs are not expected

to account for the entire difference in the measured  $\text{SO}_3$  between SAM and APXS. For some sulfur minerals detected in MSL samples, such as Ca sulfates,  $\text{SO}_3$  incompletely evolves within the SAM temperature range [2,12]. So, evolved S detected during SAM heating runs will essentially exclude most S from Ca-sulfates like gypsum or anhydrite, whereas APXS measurements will include S from those mineral phases.

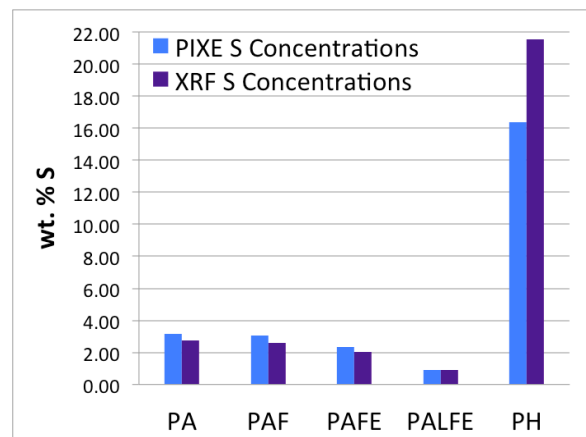


Figure 2. Uncorrected S concentrations for PIXE analyses (blue) of CBS mixtures and S concentrations in CBS mixtures calculated from XRF of individual mineral glasses (purple).

**Conclusions:** Ongoing analyses of our S-bearing mixtures will contribute to understanding the potential contribution of MPEs to differences in sample S contents derived from SAM, CheMin, and APXS measurements. Future work will involve additional mixtures with Cl-bearing phases to investigate the potential contribution of MPEs to differences in Cl abundances derived from SAM vs. APXS measurements.

**References:** [1] Grotzinger J. P. et al. (2012) *Space Science Reviews*, 170, 1–4, 5–56. [2] Sutter B. et al. (2017) *JGR Planets*, 122, doi:10.1002/2016JE005225. [3] Perrett G. M. et al. (2014) *X-Ray Spectrometry*, 43, 359–366. [4] Blake D. F. et al. (2013) *Science*, 341, doi.org/10.1126/science.1239505. [5] Yen A. et al. (2017) *GRL*, 471, 186–198. [6] Freissinet C. (2015) *JGR Planets*, 120, 495–514. [7] Vaniman D. T. et al. (2014) *Science*, 343. [8] Mertzman S. A. (2000) *Oregon Geology*, 62, 4, 99–122. [9] Eigenbrode J. L. (2016) *Personal Communication*. [10] McAdam A. C. et al. (2014) 45<sup>th</sup> LPSC Abstract #2257. [11] Ming D. W. et al. (2013) *Science Express*, doi:10.1126/science.1245267. [12] McAdam A. C. et al. (2016) 47<sup>th</sup> LPSC Abstract #2277.