

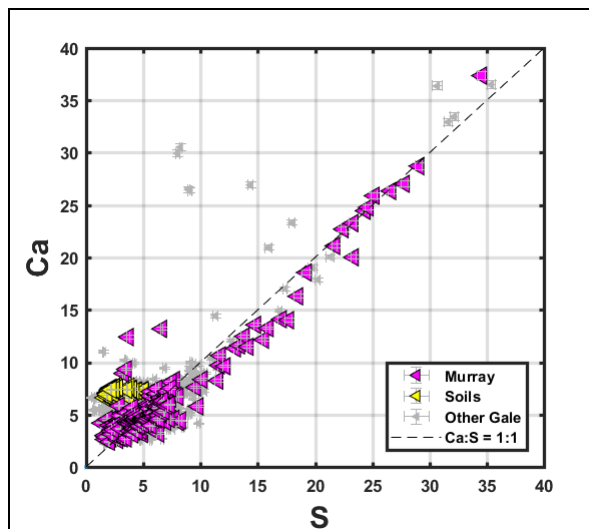
**ORIGIN AND SPECIATION OF SULFUR COMPOUNDS IN THE MURRAY FORMATION, GALE CRATER, MARS.** A. S. Yen<sup>1</sup> and R. Gellert, C. N. Achilles, J. A. Berger, D. F. Blake, B. C. Clark, A. C. McAdam, D. W. Ming, R. V. Morris, S. M. Morrison, E. B. Rampe, B. Sutter, L. M. Thompson, S. J. VanBommel, D. T. Vaniman, Others... <sup>1</sup>JPL/Caltech (Albert.Yen@jpl.caltech.edu), <sup>2</sup>Affiliation for second author (full mailing address and e-mail address).

**Introduction:** The Mars Curiosity rover has traversed nearly 20 km and gained over 350 meters in elevation since landing in Gale crater in August 2012. Through 2250 sols of surface operations, Curiosity has spent approximately 60% of its time investigating the Murray formation, a unit of layered sediments. The occurrence of sulfur compounds in the Murray formation has been established by imaging of light-toned veins by MastCam and MAHLI, chemical compositions measured by the Alpha Particle X-ray Spectrometer (APXS) and ChemCam, crystalline phase identifications by the CheMin X-ray diffractometer, and evolved gas analyses from the Sample Analysis at Mars (SAM) instrument.

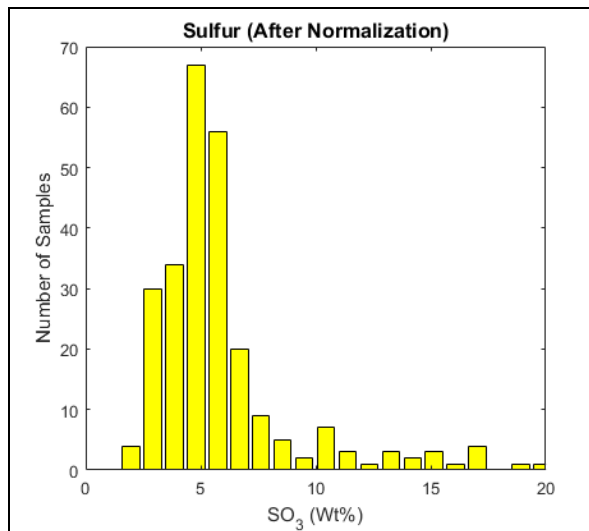
**Calcium Sulfates:** The dominant sulfur-containing compounds in the Murray formation are Ca-sulfates with quantifications (up to ~7.5 wt% total) of crystalline gypsum, bassanite, and anhydrite by CheMin. There is not enough calcium, however, to account for all the sulfur (Figs. 1, 2), and furthermore, ~2 wt% of the calcium is associated with plagioclase feldspar (~An40) in typical Murray formation samples. Calcium is also present in pyroxenes identified by X-ray diffraction. Over 400 distinct samples analyzed by the APXS have up to 5 wt% “excess” SO<sub>3</sub> after accounting for Ca-sulfate.

**Other Sulfur Compounds:** Magnesium and iron are likely cations for sulfur not associated with Ca-sulfate. With the exception of minor quantities of iron-hydroxysulfate (jarosite), no other crystalline sulfur-containing phase has been detected by CheMin. The occurrence of Mg-sulfates in selected Murray formation samples have been inferred by APXS rasters of small dendritic concretions [1,2] and Chemcam LIBS analyses of darker-toned layers [3]. However, the “excess” sulfur appears pervasive throughout the APXS analyses of the Murray formation (Figs. 1, 2) and is not restricted to specific regions. Evolved SO<sub>2</sub> further indicates the likely presence of iron sulfate/sulfide and/or Mg-sulfate in all Murray formation samples analyzed by SAM [4].

**Titanium-Referenced Gains and Losses:** The amount of SO<sub>3</sub> found by the APXS in the Murray formation ranges from less than 3 wt% to over 30 wt%. Assuming that samples with low abundance of sulfur represent the parent composition of the sediments, el-



**Fig. 1:** Molar Ca versus S for APXS analyses at Gale crater. There is more S than can be accounted for by Ca in Ca-sulfates. Including the known presence of plagioclase feldspar and pyroxenes (Ca-containing phases) exacerbates the issue of “excess” sulfur.



**Fig. 2:** Histogram of remaining SO<sub>3</sub> content for Murray formation samples after mathematical removal of Ca and S in proportions corresponding to Ca-sulfate until the remaining CaO reached 3.0 wt%. This amount of CaO represents a typical value for calcium in identified crystalline phases (plagioclase feldspar and pyroxene).

emental gains and losses can be calculated for increasing sulfur content by referencing an immobile element such as titanium. In this approach, the change in composition is given as follows for each element, X [5]:

$$\text{Gain (or loss)} = X_{\text{daughter}} - X_{\text{parent}} * (Ti_{\text{daughter}}/Ti_{\text{parent}}).$$

Using over 300 APXS measurements organized into bins of increasing sulfur content, the Ti-referenced gains and losses are calculated (Fig. 3).

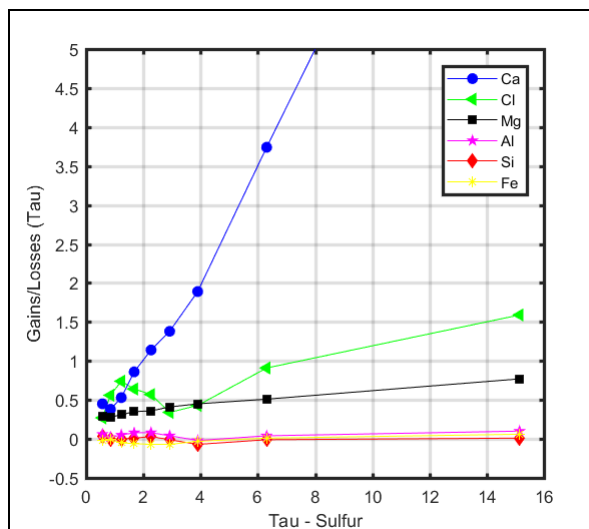
**Element Gains.** As expected, an increase in Ca is observed with increasing sulfur content (Fig. 3). An upward trend in magnesium is also evident, indicating the addition of Mg-sulfate in concert with increasing Ca-sulfate. Chlorine also appears to be a component of the fluids that introduced the sulfates.

**Element Dilution.** As the sulfur content increases, the aluminum and silicon profiles remain flat representing minimal gains or losses of these elements (Fig. 3). This is the expected result if the plagioclase feldspar component, the primary host for Al, is simply diluted by the introduction of Ca and Mg sulfates. Interestingly, the calculations also suggest minimal gains or losses of iron. This implies that the Fe-sulfates/sulfides detected by SAM were present in the samples prior to the introduction of sulfur-rich fluids or that the formation of these phases occurred in-situ and involved pre-existing Fe in the sediments.

**X-ray Amorphous Sulfur Compounds:** The excess sulfur (Fig. 2) could correspond to approximately 10 wt% sulfate, depending on the cations and hydration states. Sulfates present at these levels would be easily detectable by CheMin XRD if they were crystalline: Any Mg- or Fe-sulfates present in Murray formation samples above ~1 wt% abundance are likely X-ray amorphous.

Dehydration of most of the hydrated Mg-sulfates can produce an X-ray amorphous material [6]. An alternative process for producing X-ray amorphous Mg- and Fe-sulfates is through cryoprecipitation of sulfate-rich solutions [7]. Experiments show that freeze-drying of Mg- and Fe-sulfate solutions produce amorphous precipitates while crystalline gypsum and anhydrite are formed from Ca-sulfate solutions under similar conditions [7].

**Conclusions:** These results suggest that the fluids depositing the large amounts of Ca-sulfate to the Murray sediments also carried Mg and Cl. Mg-sulfates are likely present throughout the Murray formation as an X-ray amorphous component, either through dehydration or possibly as a product of cryoprecipitation. Any Fe-sulfates produced through fluid processes formed from pre-existing Fe, not Fe in solution.



**Fig. 3:** Titanium-referenced gains and losses for selected elements in Murray formation samples binned by increasing sulfur content. Ca, Mg, and Cl increase with the addition of S, while Si, Al, and Fe are only diluted.

**References:** [1] Yen A. S. et al. (2017) *48<sup>th</sup> LPSC*, #2253. [2] VanBommel S. J. et al. (2016) *X-Ray Spectrom.*, 45, 155-161. [3] Rapin W. et al. (2018) *49<sup>th</sup> LPSC*, #2936. [4] McAdam A. et al. (2018) P21I-3439, Fall AGU. [5] Nesbit H. W. (1979) *Nature*, 279, 206-210. [6] Vaniman D. T and S. J. Chipera (2006) *Am. Min.*, 91, 1628-1642. [7] Morris R. V. et al. (2015) *46<sup>th</sup> LPSC*, #2434.