THE SULFUR ISOTOPIC COMPOSITION OF MAGNESIUM SULFATES AT GALE CRATER. H. B.

Franz[1], A. C. McAdam[1], C. A. Knudson[1,2], J. V. Clark[3], B. Sutter[3], P. D. Archer, Jr.[3], S. P. Schwenzer[4], J. C. Stern[1], J. L. Eigenbrode[1], C. H. House[5], J. M. T. Lewis[1,6], P. R. Mahaffy[1], C. A. Malespin[1], D. J. Des Marais[7], D. T. Vaniman[8], E. B. Rampe[3]. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, [2]University of Maryland, College Park, MD 20742, [3]NASA Johnson Space Center, Houston, TX 77058, [4]The Open University, Milton Keyes MK7 6AA, UK, [5]Pennsylvania State University, University Park, PA 16802, [6]Howard University, Washington, DC 20059, [7]NASA Ames Research Center, Moffett Field, CA 94035, [8]Planetary Science Institute, Tucson, AZ 85719.

Introduction: A key orbital observation that led to the selection of Gale crater as the landing site for the Mars Science Laboratory (MSL) Curiosity rover was the presence of phyllosilicate-rich sedimentary layers overlain by sulfate-rich layers, which may reflect a global-scale environmental shift that occurred on Mars [1,2]. Because this change in environment may have affected processes associated with sulfur-bearing minerals, such as atmospheric photochemistry, deposition of sulfur at the surface, and oxidation-reduction reactions involving sulfur-bearing minerals, sulfur isotope ratios of samples from the sulfate-rich unit are important measurement targets to help understand the transition from phyllosilicate-rich to sulfate-rich sediments. Several samples acquired by drilling mudstones and sandstones in the phyllosilicate-rich (Glen Torridon or GT) region, the transition zone (TZ) from GT into the sulfate-rich unit (SU), and the SU were analyzed by the Sample Analysis at Mars (SAM) instrument suite. Sulfur released as SO_2 during evolved gas analysis (EGA) of these samples indicated variable abundances and isotopic compositions of S-bearing species (Fig. 1). We will compare sulfur isotope ratios of minerals in the SU with those in underlying sediments and discuss possible implications for formation processes and environments.

Experimental Methods: In EGA experiments, powdered solid samples, typically < 150 μm, are heated in one of SAM's pyrolysis ovens to release volatiles. SAM uses He carrier gas to sweep volatiles through the gas manifold and quadrupole mass spectrometer (QMS), with nominal pressure and flow rate of ~30 mb and ~0.8 sccm, respectively. During a nominal experiment, the sample is heated to ~850 °C at a rate of 35 °C/min. The QMS continuously samples the outflow from the pyrolysis oven, scanning over the *m/z* range of interest. Integration of the QMS signal over time for particular *m/z* allows quantitative estimates of chemical and isotopic abundance. Methods for calculation of sulfur isotope ratios ($\delta^{34}S$) are detailed in reference [3].

The temperatures at which volatiles are released during EGA provide clues to mineral phases from which they derived. In the case of sulfur, SAM observes SO_2 peaks from Fe-sulfide and Fe-sulfate degradation at temperatures of ~500-650 ⁰C. Laboratory experiments

with the SAM breadboard instrument at NASA Goddard Space Flight Center [3] indicate that some hydrated Mg-sulfates also produce a broad SO_2 peak within this temperature range, but it is accompanied by a larger peak with initiation near 800 ⁰C. This feature can help distinguish between releases from Fe- and Mg-sulfates between ~500-650 ⁰C. Degradation of Mg- and Ca-sulfates is also facilitated by catalytic activity of coexisting minerals, producing SO_2 above 700 or 800 ⁰C. This process is poorly constrained and inefficient at SAM oven temperatures, as most of these minerals in isolation, particularly Ca-sulfates, would only release SO_2 at temperatures above the SAM maximum. Thus it is likely that most SAM high-temperature SO_2 peaks, especially those starting > 800 ⁰C, represent only partial release of sulfur from sulfates and are not useful for quantification of mineral abundances. However, calibration experiments indicate that the partial release of sulfur from these peaks does not produce a measurable effect on sulfur isotope ratios obtained by SAM [3].

Because there is overlap between SO_2 peak temperatures for catalyzed Mg- and Ca-sulfate degradation, we incorporate data from Curiosity's APXS, ChemCam, and CheMin instruments into our interpretation of potential mineral sources. In some cases, we are able to distinguish between potential sulfate sources by characteristic water releases, such as the narrow peak observed for Ca-sulfates gypsum and bassanite ~160 ⁰C [4] compared to somewhat broader peaks ~200 ⁰C for polyhydrated Mg-sulfates and ~420 ⁰C for kieserite observed with the SAM breadboard instrument.

EGA Results: SO_2 releases from the samples of the GT, TZ, and SU are shown in Fig. 1. Mass estimates for samples received by SAM likely differ because of uncertainties associated with the current drilling and sample delivery technique. In addition, due to only partial degradation of Ca- and Mg-sulfates at high temperature as already described, the relative peak heights and areas under the EGA curves do not necessarily reflect the relative abundances of sulfur-bearing phases in these samples. However, sufficient QMS signal was available to calculate $\delta^{34}S$ for all SO_2 peaks.

Samples from the GT region (NT, BD, and PT) produced predominantly broad SO_2 peaks from ~400-700 ⁰C, interpreted to reflect mostly Fe-sulfates and

possly some Fe-sulfides. The NT and PT samples also produced small peaks near 800 ⁰C, suggesting minor Mg- or Ca-sulfates. Contributions from Mg-sulfate were also suggested by shoulders in the BD and PT releases near 700 ⁰C. Water releases from these samples are consistent with both Ca-sulfate, supported by CheMin detections [5], and polyhydrated Mg-sulfate.
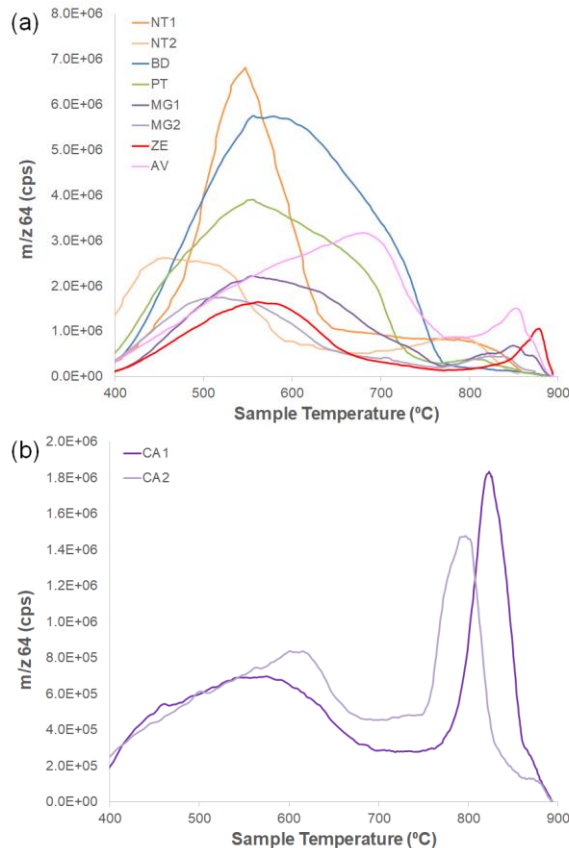

Figure 1. SO₂ released from (a) the last 3 samples drilled in the GT region (NT-PT) and the transition zone from GT to the sulfate unit (MG -ZE) and (b) the sulfate unit, shown as the QMS signal at *m/z* 64. Abbreviations in the legend indicate sample names: NT = Nontron; BD = Bardou; PT = Pontours; MG = Maria Gordon; ZE = Zechstein; AV = Avanavero; CA = Canaima. The high-temperature peaks (>700 ⁰C) likely reflect only partial degradation of sulfate sources.

Mid-temperature SO₂ releases from samples in the TZ (MG, ZE, and AV) were generally similar to those of GT, but high-temperature releases were shifted slightly upward. The mid-temperature peak maximum of AV was also higher than those of MG and ZE, suggesting differences in the chemical compositions of these sulfates. Ca-sulfates were detected by the CheMin instrument in all three samples [5] and supported by low-temperature water releases in SAM EGA.

The SO₂ release pattern from the CA sample from the SU was similar to those of MG and ZE. The CheMin instrument detected crystalline polyhydrated Mg-sulfate as well as Ca-sulfate in the CA sample [5]. The shape of the CA2 mid-temperature release suggests the presence of one or more additional phases, such as Fe-sulfate or Fe-sulfide, with peak ~600 ⁰C. The differences in peak temperatures for the high-temperature releases from AV and CA also suggest possible contributions from multiple sulfate sources that may be at abundances below the CheMin detection limit.

Discussion: Values of $\delta^{34}S$ for the GT samples shown here were similar to that of martian mantle sulfur (i.e., $\delta^{34}S$ near zero [6]), except for a small ^{34}S depletion at BD. This is consistent with previous findings for the GT region [7]. SO₂ associated with Mg- or Ca-sulfates in underlying strata has yielded near-zero or enriched values of $\delta^{34}S$ [3]. In contrast, samples from the TZ and SU have produced ^{34}S-depleted SO₂ in both mid- and high-temperature ranges. Comparison of release temperatures and $\delta^{34}S$ of SO₂ from these samples and those previously analyzed within Gale crater [3,6] suggests mixing between various sources of sulfates, with GT samples dominated by Fe-sulfates of composition similar to bulk mantle sulfur and increasing contributions from Mg-sulfates, and possibly some Fe-sulfates, with significant ^{34}S depletions through the TZ and into the SU.

Although SAM also observed significant ^{34}S depletions in a few samples reported previously [3,7], those depletions were associated with SO₂ likely from Fe-sulfide phases and were interpreted to reflect possible hydrothermal activity beneath Gale crater. It is unlikely that the same mechanism was directly responsible for the isotopic signature of the Mg-sulfates encountered in the TZ and SU, since equilibrium fractionation would favor ^{34}S depletion in sulfides and enrichment in sulfates. Possible reasons for the differences in $\delta^{34}S$ of these sulfates compared to those in underlying sediments include later oxidation of ^{34}S-depleted sulfide from a source inside or outside Gale crater, fractionation between Mg-sulfates of varying hydration states over geologic time scales [8], or a change in the predominant processing and preservation pathway for atmospheric sulfur in minerals of Mount Sharp. We will consider each of these possibilities in our presentation.

References: [1] Milliken et al. (2010) *GRL* 37. [2] Bibring et al. (2006) *Science* 312. [3] Franz et al. (2017) *Nature Geosci.* 10. [4] Sutter et al. (2022) *JGR* 127. [5] Rampe et al. (2023) *This LPSC*. [6] Franz et al. (2014) *Nature* 508. [7] Wong et al. (2022) *JGR* 127. [8] Bobocioiu and Caracas (2014) *Amer. Min.* 99.