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

Introduction: Since landing in Mars’ Gale crater in August 2012, the Mars Science Laboratory (MSL) Curiosity rover has collected numerous observations of sulfate minerals, which are ubiquitous at the planet’s surface. Compositional data from the Chemistry and Mineralogy (CheMin), Alpha Particle X-ray Spectrometer (APXS), and ChemCam instruments indicate the prevalence of Fe-, Ca-, and Mg-bearing sulfates in sediments explored by Curiosity [e.g., 1-8]. These observations are complemented by those of the Sample Analysis at Mars (SAM) instrument, which utilizes evolved gas analysis (EGA) to assess the abundance and isotopic composition of volatile compounds released through pyrolysis of solid sample materials [9].

SAM measures isotope ratios of sulfur in SO$_2$ sourced from sulfur-bearing minerals, predominantly sulfides and sulfates [10]. Sulfur isotope ratios in Gale crater sediments reflect processes occurring in magmatic, atmospheric, and aqueous environments, which have produced a range of ~70% in values of $\delta^{34}$S [10-12]. SO$_2$ associated with sulfates has exhibited an intriguing array of compositions during Curiosity’s traverse. Fe-sulfates at Gale crater have consistently shown isotopic compositions similar to that of martian mantle sulfur, with $\delta^{34}$S near zero [10-11,13]. In contrast, sulfur released from Mg- and possibly Ca-sulfates has been found to carry both enrichments and depletions in $^{34}$S, reflecting alteration of rocks that introduced sulfur affected by atmospheric and surface processes [10-12].

In October 2022, Curiosity analyzed Canaima (CA), the first sample drilled from the sulfate-rich unit detected from orbit and interpreted to reflect a global-scale environmental shift, based on the abrupt transition from phyllosilicate-rich layers that underlie it [14-15]. SAM measured S isotopic depletions in starkeyite detected by SAM and CheMin at CA [4,12] and in the transition zone between phyllosilicate- and sulfate-rich units [12] that are distinct from compositions of Mg-sulfates encountered previously in Curiosity’s traverse, which had $\delta^{34}$S near zero or enriched in $^{34}$S [10-11]. Here we report results of sulfur isotope measurements for samples in the sulfate unit stratigraphically above the Canaima drill site.

Experimental Methods: In EGA experiments, powdered solid samples, typically sieved to < 150 μm, are heated in one of SAM’s pyrolysis ovens to release volatiles, which are swept from the oven to the Quadrupole Mass Spectrometer (QMS) with He carrier gas. The nominal pressure and flow rate through SAM’s gas manifold are ~30 mb and ~0.8 sccm, respectively. During a typical 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 [10].

Volatiles peak temperatures during EGA help constrain mineral phases from which the volatiles originated. For example, Fe-sulfide and Fe-sulfate typically produce SO$_2$ peaks from ~500-650 °C under SAM operating conditions. Degradation of Mg- and Ca-sulfates usually occurs in SAM only through catalytic activity of coexisting minerals, producing SO$_2$ above 700 or 800 °C. 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 °C, represent only partial release of sulfur from sulfates and are not useful for quantification of mineral abundances [17]. 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 [10].

Samples: We will discuss data for the second and third samples acquired by Curiosity in the layered sulfate unit. Both were obtained from the Mirador formation of the Mount Sharp group. The first of these, named Tapo Caparo (TC), was located in the Marker Band, an indurated, dark-toned sedimentary sequence of extensive lateral extent embedded within the Amapari member [16]. The second, Ubajara (UB), was obtained from a sandstone of the Chenapau member above TC.

EGA Results: SO$_2$ releases from the CA, TC, and UB samples are shown in Fig. 1. SAM EGA data indicate the predominance of Fe-sulfates in both TC and UB samples, based on SO$_2$ peak temperatures ~500-600 °C. Quadratic discriminant analysis utilizing abun-
dances of multiple S-bearing compounds and δ34S values [11] supports the interpretation that SO2 evolved from these samples derived from Fe-sulfates and not Fe-sulfides. Although data from the CheMin and APXS instruments indicate the presence of Mg- and Ca-sulfates in these samples as well, SAM did not detect those minerals through SO2 evolutions, such as the pattern of isotopically depleted mid- and high-temperature peaks released from starkeyite at CA (Fig. 1), which is similar to that observed in laboratory analyses of polyhydrated Mg-sulfate with the SAM breadboard instrument [12]. However, water releases from the TC and UB samples support possible contributions from hydrated Ca- and Mg-sulfate phases. For example, pyrolysis of gypsum produces a sharp water peak around 160 °C, while starkeyite releases water over a broader temperature range of ~100-200 °C (Fig. 2). These observations suggest potential differences in sulfate crystallinity or catalytic activity of other minerals interacting with sulfates compared to previous samples.

Figure 1. SO2 released from the first three samples drilled in the sulfate unit, shown as the QMS signal at m/z 64. Abbreviations in the legend indicate sample names: CA = Canaima; TC = Tapo Caparo; UB = Ubajara.

Discussion: SO2 evolution temperatures and values of δ34S for the samples shown here indicate the presence of Fe-sulfate with isotopic compositions similar to that of martian mantle sulfur (i.e., δ34S near zero), consistent with Fe-sulfates encountered throughout Curiosity’s traverse. This composition contrasts the strong δ34S depletions observed in Mg-sulfates of underlying sulfate unit layers and the transition zone from phyllosilicate-rich layers that preceded it. We previously explored possible mechanisms for producing the depleted compositions of starkeyite at CA, including redox chemistry or Mg-sulfate hydration-dehydration cycles [12,19].

Because SAM did not observe SO2 released from Mg-sulfates in TC or UB, despite the presence of small amounts of Mg-sulfates detected by CheMin, it is not possible to compare compositions of Mg-sulfates here with those analyzed previously. However, the differences in SO2 evolution profiles and δ34S values of these samples compared to those of CA and samples in the transition zone suggest a change in sulfate formation and alteration environments from the base layers of the sulfate unit into the Marker Band and beyond. These observations are consistent with hypotheses proposing that the sulfate layers within Mount Sharp record a history of environmental change on Mars [14-15].