X-RAY AMORPHOUS SULFUR-BEARING PHASES IN SEDIMENTARY ROCKS OF GALE CRATER, MARS. R. J. Smith1, S. M. McLennan1, E. Dehouck2, E. B. Rampe3, B. Sutter4, K. L. Siebach5, B. H. N. Horgan6, V. Sun7, A. McAdam8, N. Mangold9, D. Vaniman10, M. Salvatore11, M. T. Thorpe12, C. N. Achilles8, T. Gabrielse13, and S. Czarnecki14, 1Stony Brook University, USA (rebecca.j.smith@stonybrook.edu), 2Université Lyon1, France, 3NASA Johnson Space Center, USA, 4Jacobs JETS at NASA Johnson Space Center, USA, 5Rice University, USA, 6Purdue University, USA, 7Jet Propulsion Laboratory, California Institute of Technology, USA, 8NASA Goddard Space Flight Center, USA, 9Université de Nantes, France, 10Planetary Science Institute, USA, 11Northern Arizona University, USA, 12Texas State University, USA, 13U.S. Geological Survey, USA, 14Arizona State University.

Introduction: The Curiosity rover in Gale crater is currently investigating a mineral transition observed from orbit (clay-rich to sulfate-rich rocks; Fig. 1) [e.g., 1-2]. This spectrally deduced mineral transition has been noted at other locations on Mars [e.g., 3] and is thought to indicate global-scale climate change [1]. To fully appreciate the importance of this transition, it is necessary to investigate the sulfur (S)-bearing phases along the rover traverse and into the transition.

The rover instrument suite suggests the presence of crystalline and amorphous S-bearing phases that may be distinct from each other. For rocks below the observed transition, CheMin X-ray diffraction (XRD) and ChemCam chemical data indicate mostly crystalline Ca-sulfates associated with diagenetic features and cements, with minor Fe-sulfates [4-5]. Evolved gas analyses (EGA) from the SAM instrument indicate mostly Fe- and Mg-sulfates and/or sulfites in the bedrock [6-7]. Since CheMin did not detect Mg-, and in some cases, Fe-S phases, these phases are either crystalline but present in abundances below CheMin detection limits (~1 wt%) or X-ray amorphous in nature. Mass balance calculations indicate most rocks have some fraction of their bulk SO\(_3\) in the X-ray amorphous component [e.g., 8-9].

Here, we characterize the abundances and compositions of the X-ray amorphous S-bearing phases in most of the rocks examined by CheMin below the mineral transition. We then speculate on the nature and identity of these phases and discuss implications for past environments in Gale crater.

Methods: We use bulk X-ray amorphous component compositions from [9] for all rock samples through Vera Rubin ridge (VRR, Fig. 1). Bulk X-ray amorphous component compositions are estimated through mass balance where bulk crystalline compositions (CheMin-derived minerals and abundances) are subtracted from bulk sample chemistry (APXS).

We also use SAM SO\(_3\) EGA data for five of the nineteen samples in this study that have relatively high X-ray amorphous SO\(_3\) contents (CH, BS, GH, MJ, and WJ). Peaks were fit to the SO\(_3\) EGA traces and were then assigned to Mg-S and Fe-S phases; peak areas were used to determine abundances. Assuming SAM measures all S-bearing phases except Ca-sulfates [7], we attribute any difference between APXS and SAM-derived SO\(_3\) contents to amorphous Ca-sulfate (after subtracting contributions from crystalline Ca-sulfates).

SAM EGA method uncertainties result from: (1) SAM SO\(_3\) abundances are relatively low (< 7 wt%) and can have relatively high uncertainties (up to 3 wt%) [7]; (2) the methods assume that APXS, CheMin, and SAM measure the exact same sample but this is not completely true; (3) when a peak fell within temperature ranges shared by Mg-S and Fe-S phases, we calculated a range of abundances, first by ignoring the ambiguous peak altogether, next by attributing the peak solely to Mg-S, then Fe-S phases.

Results: On average, bulk rocks contain ~5.3 wt% crystalline SO\(_3\) (standard deviation = 4.4 wt%; range = 0.66 - 14.1 wt%) and ~4.2 wt% amorphous SO\(_3\) (standard deviation = 2.6 wt%; range = 0.19 – 9.9 wt%). Overall, between 20 and 90% of any sample's SO\(_3\) content is in the X-ray amorphous state.

A SO\(_3\)-MgO-CaO ternary diagram (Fig. 2) helps characterize potential compositions of the amorphous S-bearing material at each drill site. Most of the X-ray
amorphous components plot over a range consistent with complex/variable mixtures of amorphous and poorly crystalline Ca-, Mg-, and Fe-sulfates with other Mg- and Ca-bearing phases (e.g., silicates).

The evolved S\textsubscript{O}\textsubscript{2} trace analyses (Fig. 3) indicate Mg-S in all five samples, and all would have Mg-sulfates of e.g. kieserite composition at or above CheMin’s detection limit (average = 4.10 wt%) but CheMin did not detect Mg-S phases. Likewise, all five contain Fe-S phases. Jarosite was detected by CheMin in two of the samples (CH and MJ2), and in both cases EGA data indicates more SO\textsubscript{3} related to Fe-S phases than the jarosite can account for. In all SAM analyzed samples presented here, except CH, X-ray amorphous Mg-S phases are more abundant than Fe-S phases. Yet, some samples analyzed by SAM not in this study indicate more Fe-S than Mg-S and so a more detailed study is necessary.

Three of the five samples examined in this study with SAM data (MJ, BS and GH) do not have enough crystalline Ca-sulfates to account for the difference between APXS and SAM measurements, and so the remaining SO\textsubscript{3} was attributed to amorphous Ca-sulfates.

There is no systematic change in X-ray amorphous SO\textsubscript{3} content with stratigraphic position, as was observed for X-ray amorphous SiO\textsubscript{2} contents [9], and there is no strong trend in X-ray amorphous S-bearing phase composition with stratigraphic group. Overall, X-ray amorphous SO\textsubscript{3} is likely present as complex mixtures of Mg-, Fe-, and possibly Ca-sulfate phases.

**Discussion:** Amorphous sulfates have been previously hypothesized for the Martian surface because hydrated Mg- and Fe-sulfates structurally destabilize once exposed to the temperatures and relative humidity of the modern Martian surface or inside CheMin [11-13]. Still, while gypsum could dehydrate to bassanite and possibly anhydrite under Mars surface conditions [4], it is unlikely for Ca-sulfates to become amorphous through dehydration. More work is needed to confirm the presence of X-ray amorphous Ca-S phases and to understand their formation mechanisms.

Many of the crystalline Ca-sulfate detections along the traverse have been associated with observable diagenetic features that crosscut the bedrock [e.g., 4], and sharp contacts between mineral infilling and host rock indicate that late-stage diagenetic fluids were primarily confined to fractures and did not permeate the surrounding bedrock [14]. It is likely that the amorphous sulfates predate the Ca-sulfate features, and could contribute to sediment cementation.

**Implications:** Gale crater sedimentary rocks below the clay-sulfate transition contain Mg-S phases, most likely Mg-sulfates mixed with Fe- and Ca-sulfates that appear X-ray amorphous. Why do the rocks higher up in the “sulfate unit” have much stronger hydrated Mg-sulfate spectral signatures from orbit? Does this relate to an overall increase in Mg-sulfate abundance, an increase in Mg-sulfate hydration or crystallinity, a decrease in clay-mineral abundances, or a combination of these factors [15]?

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**Fig. 2.** X-ray amorphous SO\textsubscript{3}-MgO-CaO (molar) from the mass balance method [9]. Crystalline Mg-, Ca-, and Fe-S phases (squares) shown for comparison and inset figure helps interpret mixing.

**Fig. 3.** SAM SO\textsubscript{3} attributed to Mg-S and Fe-S (jarosite removed) phases. Bars represent abundance ranges (see text).

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**References:**