ASSESSING THE PERFORMANCE OF TMAH THERMOCHEMOLYSIS ON MG-SULFATE MARS-ANALOG STANDARDS. P. C. Gant[1] and A. J. Williams[1], [1]Department of Geological Sciences, University of Florida, 241 Williamson Hall, PO Box , 112120 Gainesville, FL 32611 (pgant@ufl.edu)

Introduction: The NASA Mars Curiosity Rover landed in Gale crater, Mars, in 2012 with the goal of searching for past or present habitable environments on the Red Planet [1]. One instrument aboard the rover that can detect organic carbon compounds is the Sample Analysis at Mars (SAM) instrument suite. The instrument suite is comprised of a Quadruple Mass Spectrometer (QMS), a Gas Chromatograph (GC), and a Tunable Laser Spectrometer (TLS). The GC and QMS work in tandem to separate and identify organic compounds.

At launch, SAM was equipped with 74 sample cups. Of those cups, 9 are reserved for wet chemistry and use either the MTBSTFA reagent (7 cups) or TMAH reagent (2 cups). One TMAH experiment has already been performed at the Mary Anning drill site in the Glen Torridon region on Mars [2]. There are several questions that remain upon analyzing the data from that experiment. The source of the organics identified in that experiment are likely abiotic, derived from exogenous (e.g meteoritic input) or endogenous (geologic sources), although biotic sources cannot be ruled out. Additionally, another source for some of the organics discovered could be from the SAM instrument itself. There is a possibility that the hydrocarbon trap creates byproducts when heated, providing a source for some of the organics found in the sample [3].

There is only one TMAH experiment remaining on SAM and it is imperative to optimize the experiment to best utilize the remaining TMAH wet chemistry cup. Knowing the mineralogy of the ideal sample, the appropriate pyrolysis temperature for thermochemolysis, and knowing the potential byproducts produced internally within the experiment will all help the MSL team to determine the best location and experimental design to run the final TMAH wet chemistry experiment.

The Curiosity rover is currently located within the sulfate bearing unit of *Aeolis Mons*. Orbital imagery and spectroscopy show that within the sulfate bearing unit, there are iron oxides, poly-hydrated magnesium sulfates, and clays [4]. The goal of this task is to understand how Mg-sulfate samples will behave under SAM-like-pyro-GC-MS conditions. Knowing the temperature that the Mg-sulfate salts decompose is a primary objective for this activity.

We hypothesis that TMAH thermochemolysis will liberate organics in Mg-sulfates at a lower temperature than neat pyrolysis.

Methods: The use of a derivatization or thermochemolysis agent allows polar compounds to be analyzed with gas chromatography by increasing the volatility of those molecules [5]. The reagents available on SAM are N-methyl-N-(tertbutyldimethylsilyl) trifluoroacetamide (MTBSTFA) in dimethylformamide (DMF) and tetramethylammonium hydroxide (TMAH) in methanol. To test our hypothesis, TMAH thermochemolysis was performed on commercial Mg-sulfate standards. The standards that this study will focus on are epsomite and an anhydrous reagent $MgSO_4$. The standards were powdered, pyrolyzed, and analyzed with GC-MS. One of the goals is to assess which pyrolysis temperature is optimal for these $MgSO_4$ standards, therefore the samples were analyzed with pyrolysis temperatures of 550˚C, 875˚C, and 975˚C. The samples were analyzed on an Agilent 7890B-5977 GC-MS coupled to a Frontier 3030D pyrolysis oven, using a 30m Restek MXT-5 capillary column with a 0.25 mm internal diameter and He as the carrier gas. The samples underwent flash pyrolysis at the three specified temperatures. followed by a chromatographic separation with the GC oven starting at 50˚C then ramping at 15˚C/min to 300˚C with a 5-minute hold. The samples were prepared by combining 1 mg of powdered sample with 1 µL of TMAH in methanol. In addition to neat pyrolysis and TMAH thermochemolysis, the samples were also analyzed with a SAM-like ramp of 35˚C/min. The samples and testing conditions can be found in Table 1.

	$MgSO_4$ (Anyhydrous)	**Epsomite ($MgSO_4 \cdot 7H_2O$)**
Pyrolysis	Neat	Neat
Temperature	550C, 875C, 975C	550C, 875C, 975C
Thermochemolysis	TMAH	TMAH
Temperature	550C	550C
SAM Ramp	TMAH + 35C/min	TMAH + 35C/min

Table 1. Standard compositions and testing conditions used within this study.

Results and Interpretations: The chromatograms below are a representative sample of the two samples tested with TMAH at 550˚C vs TMAH with a SAM-like ramp of 35˚C/min.

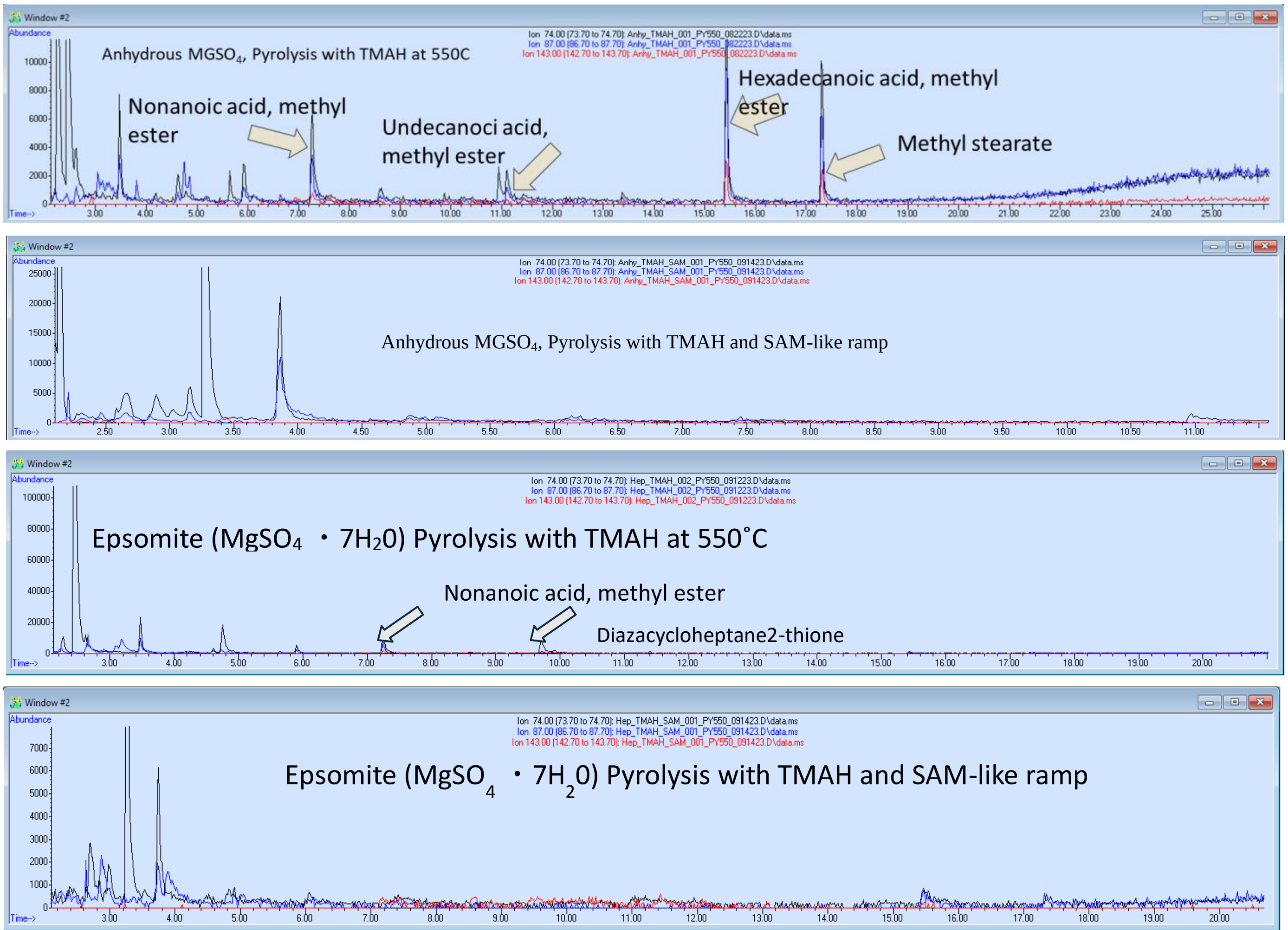

Figure 1. Comparison of anhydrous $MgSO_4$ either flash pyrolyzed with TMAH at 550˚C (top) or pyrolyzed with TMAH up to 550C using a SAM-like 35˚C/min ramp. The chromatograms demonstrate that the SAM-like ramp did not perform as well as flash pyrolysis alone at liberating organics from the Mg-sulfate commercial samples.

Conclusions: The Mars Curiosity Rover is currently exploring the sulfate bearing strata of Gale crater. Only one of the two TMAH wet chemistry cups remain after completing the first experiment at the Mary Anning drill hole in the Glen Torridon unit of Gale crater. There are several questions that remain that this work seeks to answer, primarily around the optimization of the experimental design. The central hypothesis to this work is that TMAH thermochemolysis will liberate organics in Mg-sulfates at a lower temperature than neat pyrolysis. To test this hypothesis, TMAH thermochemolysis will be performed on commercial Mg-sulfate standards. The results from this experiment will provide valuable information to how Mg-sulfate minerals will behave under SAM-like conditions, so their performance on Mars can be predicted, lending confidence to the optimization of the second and final TMAH experiment.

References: [1] Grotzinger, J.P. et al., (2012) Space science reviews, 170, pp.5-56. [2] Millan, M. et al., (2022). JGR: Planets, 127(11), p.e2021JE007107. [3] Buch, A. et al (2019) JGR 124, 2819-2951. [4] Vaniman, D.T. et al., (2004) Nature, 431(7009), pp.663-665. [5] Mahaffy, P.R. et al., (2012). *Space Science Reviews*, 170, pp.401-478.