

COMBINED THERMAL AND EVOLVED GAS ANALYSIS, X-RAY DIFFRACTION, VIS-NIR, X-RAY FLUORESCENCE, AND DUV RAMAN SPECTROSCOPY OF SYNTHETIC AMORPHOUS MAGNESIUM SULFATES AND STARKEYITE: IMPLICATIONS FOR THE DETECTION OF MG SULFATES BY THE SAMPLE ANALYSIS AT MARS INSTRUMENT IN GALE CRATER, MARS. J.V. Clark¹, R.V. Morris², N.C. Haney³, R.S. Jakubek³, P.D. Archer³, A.C. McAdam⁴, B. Sutter³, H. Franz⁴, J. Lewis^{4,5,6}, J. Berger³, S. Chipera⁷, S. A. Mertzman⁸, C. Malespin⁴. ¹GeoControls Systems Inc – Jacobs JETSII Contract at NASA Johnson Space Center, Houston, TX, 77058. ²NASA Johnson Space Center, Houston, TX, 77058. ³Jacobs JETSII Contract at NASA Johnson Space Center, Houston, TX, 77058. ⁴NASA Goddard Space Flight Center, Greenbelt, MD, 20771. ⁵Department of Physics and Astronomy, Howard University, Washington, D.C., 20059. ⁶Center for Research and Exploration in Space Science and Technology, Greenbelt, MD, 20771. ⁷Planetary Science Institute, Tucson, AZ, 85719. ⁸Department of Earth and Environmental, Franklin and Marshall College, Lancaster, PA, 17604.

Introduction: The *Curiosity* rover is exploring a region in Gale crater, Mars, that has orbital spectral data consistent with the presence of hydrated Mg sulfates [e.g., 1]. Investigating the sulfate mineralogy of the sulfate-bearing region is important for understanding a potential shift from wet to arid climate in martian history. Sample Analysis at Mars-Evolved Gas Analyzer (SAM-EGA) data are critical for interpreting the Mg sulfates in Gale because APXS and CheMin analyses indicate that they are mixed crystalline and amorphous materials [2-4] that need further characterization. The primary goal of this study was to prepare to interpret the presence and types of Mg sulfates in the sulfate-bearing region using SAM-EGA data.

Two, widely cited [e.g., 5, 6] potential Mg sulfates, starkeyite ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) and X-ray amorphous Mg sulfate, were synthesized and then analyzed on a SAM-EGA analog instrument. XRD, Vis-NIR, and XRF data were collected to support mineralogical interpretations of the synthesized minerals. Additionally, the synthetic samples were analyzed with a Mars 2020 rover SHERLOC analog deep-UV (DUV) Raman to assist in future investigations of sulfates in Jezero crater, Mars.

Methods: Starkeyite synthesis was completed by heating epsomite (synthetic; CVS) in air at 47 °C for ~78 hrs [7]. Amorphous Mg sulfates were synthesized via rapid desiccation of the synthetic epsomite and an epsomite-rich natural sample (HWKD212). Rapid desiccation of the epsomite samples was done by heating on a hot plate at ~100 °C for ~3 days in a N_2 filled glove box with a relative humidity (RH) of ~0.3% at ~25 °C.

Synthesized amorphous Mg sulfates and starkeyite were analyzed by XRD (Rigaku Miniflex 6G) by immediately transferring the samples from the oven or glove box to the XRD instrument (~1 min transfer time). Each individual sample was analyzed by XRD three consecutive times, with each analysis taking ~27 minutes, with the goal of detecting crystallinity and/or hydration changes upon exposure to air over time.

The same samples were analyzed on a thermal gravimeter (TG)/differential scanning calorimeter (DSC) connected to a quadrupole mass spectrometer, configured to operate similarly to the SAM-EGA. The purpose of these analyses was to assess water content and

SO_2 release profiles and to compare to the SAM-EGA data from recent and future Gale crater samples. Samples were transferred from the oven or glove box and immediately analyzed with the following parameters: maximum temperature of 1300 °C, a heating rate of 35 °C/min, furnace pressure of 30 mbar, and He flow rate of 10 sccm.

In addition, the natural sample was analyzed for chemistry by XRF, and all samples were analyzed by Vis-NIR (ASD FieldSpec 3) and DUV Raman spectroscopy (ACRONM, a custom SHERLOC analog instrument) to provide broader, mission-relevant characterization. Vis-NIR spectra were obtained under desiccating conditions, and Raman spectra were obtained in the same manner as XRD patterns.

Results and Discussion: Vis-NIR spectra of synthetic Mg sulfates and kieserite were distinct from each other due to differences in hydration. Synthetic starkeyite did not show detectable changes in crystallinity or hydration over the course of ~1.5 hours of XRD analysis (Fig. 1). Exposure to lab air overnight, however, caused the synthetic starkeyite to rehydrate to epsomite. Starkeyite TG and EGA results showed a 37.5% weight loss that tapered off at ~385 °C and was consistent with 4 waters (Figs. 1 and 2). Within the broad water release was a smaller, sharp water release at ~300 °C (Fig. 2), which corresponded with an exotherm in the DSC data. Starkeyite produced an SO_2 release peak at 1043 °C.

Synthetic amorphous Mg sulfates did not become crystalline with air exposure over the course of ~1.5 hours, based on XRD results (Fig. 1). Air exposure overnight resulted in crystallization and rehydration to epsomite. TG data from the amorphous Mg sulfates were consistent with <1 waters (Fig. 1). The synthetic amorphous Mg sulfates did not exhibit broad low temperature water releases like the starkeyite, but did produce sharp water releases ~305 °C which corresponded to exotherms. The amorphous Mg sulfate sample (from synthetic epsomite) produced an SO_2 release peak at 1045 °C, similar to starkeyite. The HWKD212-derived amorphous Mg sulfate sample produced two SO_2 releases: a smaller one with a peak at ~750 °C and a larger one with a peak ~968 °C (Fig. 2).

The ~750 °C SO₂ release may be attributed to the presence of amorphous Al-bearing sulfate, as inferred from the HWKD212 bulk composition (Fig. 1).

Our results suggest the high temperature (>800 °C) SO₂ release in the Mars Science Laboratory (MSL) Canaima (CA) drill sample [7], representing the base of the sulfate-bearing unit in Gale crater, may be caused by partial Mg sulfate decomposition. The SO₂ peak in CA was lower than the Mg sulfates analyzed in the lab (Fig. 2), possibly due to catalytic effects from other minerals and/or the heating ramp shutting down, which would cease evolution of SO₂ before its true peak. The amorphous Mg sulfates and starkeyite were not distinct from each other in terms of evolved SO₂ at high temperatures. Additionally, starkeyite was not distinct from other hydrated crystalline Mg sulfates (e.g., epsomite) in terms of its low temperature water release profile. If present in a SAM sample, the smaller sharp peak ~300 °C released from amorphous Mg sulfates or starkeyite would likely be obscured.

DUV Raman spectra of the Mg sulfates showed that the ν₁ band Raman shift for starkeyite and our XRD amorphous Mg-sulfates are at ~998 cm⁻¹ and ~1034 cm⁻¹, respectively (Fig. 1). ACRONM results for starkeyite and the amorphous Mg sulfates provide a reference for SHERLOC in its exploration of Jezero crater.

References: [1] Milliken *et al.*, (2010) *GRL*, 37. [2] Berger *et al.*, (*this meeting*). [3] Simpson *et al.*, (*this meeting*). [4] Rampe *et al.*, (*this meeting*). [5] Vaniman *et al.* (2004) *Nature* 431, 663. [6] Wang *et al.* (1016) *JGR-*

Planets 121, 678. [7] Grevel *et al.* (2012) *Astrobiology*, 12. [8] Clark *et al.*, (*this meeting*).

Fig. 2.. H₂O (m/z 18 for lab samples; m/z 19 for CA1 and CA2) and SO₂ (m/z 64) releases from synthesized amorphous Mg sulfates and starkeyite, both compared to CA1 and CA2. CA1 and CA2 are subsamples from the same drill hole.

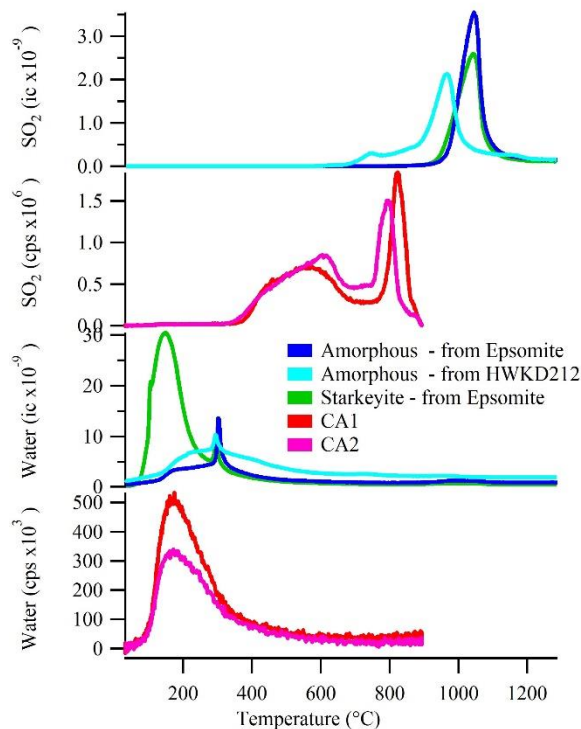


Fig. 1. Laboratory results from synthetic amorphous Mg sulfates, synthetic starkeyite, and kieserite. (a) XRD patterns, (b) TG sample weight loss and corresponding hydration state, (c) Vis-NIR spectra, (d) XRF and ACRONM Deep-UV Raman results.

