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SAMPLE ANALYSIS AT MARS-EVOLVED GAS ANALYSIS (SAM-EGA) RESULTS FROM THE CLAY-SULFATE TRANSITION REGION IN GALE CRATER, MARS. J.V. Clark¹, B. Sutter², G. Wong³, J. Lewis^{4,5,6}, A. C. McAdam⁵, P.D. Archer², P. Mahaffy⁵, H. Franz⁵, J. Eigenbrode⁵, C. Freissinet⁷, J. Stern⁵, D. Glavin⁵, A. Steele⁸, C. Knudson^{5,9,10}, C. H. House³, C. Malespin⁵, D. W. Ming¹¹. ¹Geocontrols Systems – Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, ²Jacobs JETS Contract at NASA Johnson Space Center, Houston, TX 77058, ³Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, ⁴Department of Physics and Astronomy, Howard University, Washington, D.C., ⁵NASA Goddard Space Flight Center, Greenbelt, MD 20771, ⁶Center for Research and Exploration in Space Science and Technology, Greenbelt, MD, ⁷LATMOS-IPSL/CNRS, Guyancourt, France, ⁸Carnegie Institute for Science, Washington, D.C. 20015, ⁹University of Maryland, College Park, MD, ¹⁰CRESST II, Greenbelt, MD ¹¹NASA Johnson Space Center, Houston, TX 77058.

Introduction: The *Curiosity* rover is traversing towards a region in Gale crater, Mars that has orbital spectral data consistent with the presence of sulfates [e.g., 1]. The underlying region, the “Glen Torridon” (GT) trough, has orbital spectral and *in-situ* data consistent with the presence of phyllosilicates [2]. Exploring the transition between the clay-bearing rocks in the GT region and the stratigraphically higher sulfate-bearing unit is a major mission milestone because it represents an ancient environmental and climatic change from a wet, near-neutral pH Mars to a drier and possibly more acidic planet. Here, we use Sample Analysis at Mars-Evolved Gas Analysis (SAM-EGA) data to assess chemical and mineralogical changes from the GT to the clay-sulfate transition region in order to determine if *Curiosity* is entering the sulfate-bearing unit as suggested by orbital spectral data.

Methods: *Curiosity* analyzed five sedimentary rock drill samples with its instrument suite – Nontron (NT), Bardou (BD), Pontours (PT), Maria Gordon (MG), and Zechstein (ZE) – in the upper GT and clay-sulfate transition region as of December 2021 in order to constrain their volatile chemistry and support mineralogical interpretations. NT was drilled in a rubbly mudstone unit close to the base of the Mont Mercou cliff in the Glasgow member of the Carolyn Shoemaker formation, which was in the upper GT region. BD was drilled at the top of Mont Mercou, at the border between the GT region and the clay-sulfate transition region, to assess direct stratigraphic changes in mineralogy and chemistry. Additionally, BD was sampled in an area containing sandstones rather than mudstones. PT, MG, and ZE were drilled at ~25 vertical meter intervals, and were all sampled in rocks with heavy diagenetic overprints and indeterminate grain sizes. PT, MG, and ZE were all sampled within the clay-sulfate transition region.

All five samples were analyzed by SAM-EGA by heating samples up to ~900 °C (~35 °C/min; 0.8 sccm He carrier gas). The SAM quadrupole mass spectrometer (QMS) detected evolved gases (e.g., H₂O, O₂, SO₂,

CO₂) at characteristic temperatures that were diagnostic of particular phases (e.g., sulfates, phyllosilicates, organic-C).

Results and Discussion: NT, BD, PT, and MG evolved low-temperature (<~300 °C) H₂O similar to samples in the lower GT region (Fig. 1). The two low-temperature H₂O peaks (~180 °C and ~270 °C) were consistent with adsorbed water, hydrated salts (e.g., gypsum, bassanite), and hydrated amorphous phases. The first low-temperature H₂O peak was most intense in ZE due to the high abundance of gypsum (~22 wt.%; [3]). The second low-temperature H₂O peak was likely present in ZE, however it was obscured by the more intense, lower temperature H₂O peak.

NT and BD evolved mid-temperature H₂O peaks similar to lower GT samples, however these peaks were minimal or absent in the stratigraphically higher samples (PT, MG, and ZE) (Fig. 1). These mid-temperature H₂O releases were attributed to the dehydroxylation of a dioctahedral smectite such as nontronite. The disappearance of the mid-temperature H₂O peak in the transition samples was consistent with a decrease in phyllosilicates, which was also observed in X-ray diffraction data from the Chemistry and Mineralogy (CheMin) instrument [3].

All five samples evolved broad SO₂ releases consistent with Fe sulfates, which were also detected in lower GT samples. NT2 and the stratigraphically higher samples (PT, MG, ZE) evolved high-temperature SO₂ peaks consistent with Mg sulfate (Fig. 2). This peak was especially prominent in the uppermost sample, ZE. The Fe and Mg sulfate in these samples likely occurred in the amorphous component because they were not detected as a crystalline phase by CheMin [3]. Crystalline Ca sulfate was detected in all five samples by CheMin and indirectly detected by the Alpha Proton X-ray Spectrometer (APXS) [3,4]; however Ca sulfate thermally decomposes >900 °C and is not detectable by SAM. Additionally, δ³⁴S values calculated from the SO₂ releases were more negative in ZE and MG than in stratigraphically lower samples (PT, BD,

and NT). This could be due to differences in sulfur sources in the stratigraphically higher samples.

The CO_2 evolutions detected by SAM were generally variable between sample analyses, suggesting C-species heterogeneity within the region as well as within individual drill samples. Evolved CO_2 was consistent with oxidized organic-C, though evolved CO_2 above 400°C could have contributions from carbonates.

All samples evolved mid-temperature CO peaks $\sim 375^\circ\text{C}$ and NT2 and up-section samples evolved an additional CO peak $\sim 800^\circ\text{C}$. The mid-temperature CO releases were similar between all samples and were attributed to instrument background, oxalates, or incomplete combustion of organics. The high-temperature CO releases ($\sim 800^\circ\text{C}$) observed in NT2, PT, MG1, and ZE were consistent with Mg sulfate-bound organics or refractory organics. The increase in the high-temperature CO release in up-section samples is another distinct change throughout the clay-sulfate transition.

No O_2 was detected in these samples, suggesting that oxychlorines were not present. Nitrate (NO) was either absent or present in low abundances. Broad HCl releases were observed in all samples and suggested the presence of chlorides.

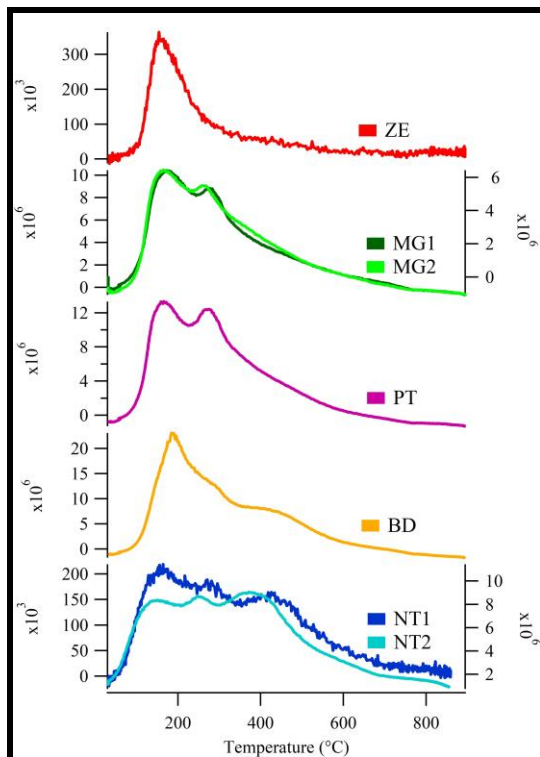


Fig. 1. H_2O (m/z 17; m/z 19 for NT1) releases from samples drilled throughout the upper GT and clay-sulfate transition region. Units in counts per second.

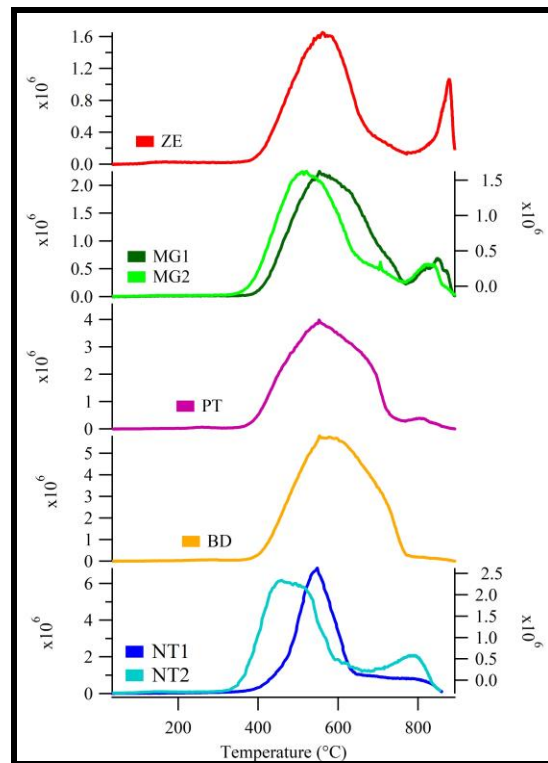


Fig. 2. SO_2 (m/z 64) releases from samples drilled throughout the upper GT and clay-sulfate transition region. Units in counts per second.

Conclusion: SAM-EGA data were used to determine if *Curiosity* was entering the clay-sulfate transition region. The decrease in mid-temperature H_2O and increase in high-temperature SO_2 in stratigraphically higher samples suggested the disappearance of phyllosilicates and re-appearance of Mg sulfates, respectively, in the transition region. S isotopes in up-section samples (MG and ZE) were also anomalously negative, suggesting a different S source than upper GT (NT) and border/transition (BD, PT) samples. Additionally, the appearance of high-temperature CO peaks in NT2 and up-section samples was consistent with refractory organics or Mg sulfate-bound organics because they overlapped with SO_2 peaks from Mg sulfate decomposition. Evolved CO_2 was variable between samples and was consistent with carbonates and oxidized organics. Overall, SAM-EGA data in the clay-sulfate transition region agree with orbital spectral data and suggest that *Curiosity* is approaching the sulfate-bearing unit. SAM-EGA data also support that idea that this transition region records a major environmental and climatic shift in martian history.

[1] Milliken et al. (2010) *GRL*, 37. [2] Bristow et al. (2021) *Science*, 373. [3] Rampe et al. (2022) *53rd LPSC*. [4] Berger et al. (2022) *53rd LPSC*.