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MINERALOGICAL AND CHEMICAL CHANGES IN THE CLAY-SULFATE TRANSITION REGION AS DETECTED BY THE SAMPLE ANALYSIS AT MARS-EVOLVED GAS ANALYZER (SAM-EGA) IN GALE CRATER, MARS. J.V. Clark¹, B. Sutter², J. Lewis^{3,4,5}, A. C. McAdam⁴, P.D. Archer², H. Franz⁴, J. Eigenbrode⁴, G. Wong⁶, L. Chou^{4,7}, C. Freissinet⁸, J. Stern⁴, D. Glavin⁴, A. Steele⁹, C. Knudson^{4,10,11}, C. H. House⁶, C. Malespin⁴, P. Mahaffy⁴, D. W. Ming¹². ¹Geocontrols Systems – Jacobs JETSII Contract, NASA Johnson Space Center, Houston, TX 77058, ²Jacobs JETSII Contract at NASA Johnson Space Center, Houston, TX 77058, ³Department of Physics and Astronomy, Howard University, Washington, D.C., ⁴NASA Goddard Space Flight Center, Greenbelt, MD 20771, ⁵Center for Research and Exploration in Space Science and Technology, Greenbelt, MD, ⁶Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, ⁷Georgetown University, Washington, D.C. 20057, ⁸LATMOS-IPSL/CNRS, Guyancourt, France, ⁹Carnegie Institute for Science, Washington, D.C. 20015, ¹⁰University of Maryland, College Park, MD, ¹¹CRESST II, Greenbelt, MD ¹²NASA Johnson Space Center, Houston, TX 77058.

Introduction: The *Curiosity* rover is exploring 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 evidence and *in-situ* detections of phyllosilicates [2]. The transition between the clay-bearing rocks in the GT region and the stratigraphically higher sulfate-bearing region may represent 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 throughout the clay-sulfate transition region with the goal of ground-truthing orbital data and testing the hypothesis of an environmental change in Gale crater’s history.

Methods: *Curiosity* analyzed 7 sedimentary rock drill samples with its instrument suite from the top of the GT region to the base of the sulfate-bearing region – Nontron (NT), Bardou (BD), Pontours (PT), Maria Gordon (MG), Zechstein (ZE), Avanavero (AV), and Canaima (CA) – in order to constrain their volatile chemistry and support mineralogical interpretations made by the Chemistry and Mineralogy (CheMin) instrument. NT was drilled in a faintly laminated mudstone close to the base of the Mont Mercou cliff in the upper GT region. BD was drilled in a sandstone at the top of Mont Mercou, at the border between the GT region and the clay-sulfate transition region. PT was sampled in a rock with heavy diagenetic overprints and indeterminate grain size. MG, ZE, and AV were drilled in cross-stratified sandstones. CA was sampled from a finely laminated sandstone, at what is interpreted as the base of the sulfate-bearing region in the Marker Band valley. A blank was analyzed between the ZE and AV samples in order to assess possible contributions from instrument background. The blank was analyzed from a cup containing residue of the Windjana sample, which had been heated to ~870 °C multiple times.

All 7 samples were analyzed by heating samples to ~870 °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).

Results and Discussion: NT, BD, PT, MG, AV, and CA evolved low-temperature (<300 °C) H₂O (Fig. 1), which was consistent with adsorbed water, hydrated salts (e.g., gypsum, hydrated Mg sulfates), 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], and possibly obscured other low-temperature water releases.

NT and BD evolved mid-temperature H₂O peaks (~375-500 °C), however these peaks were minimal or absent in the stratigraphically higher samples (PT through CA; 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 and CA was consistent with a decrease in phyllosilicates, which was also observed in X-ray diffraction data from CheMin [3].

All 7 samples evolved broad SO₂ releases (~575 °C) consistent with Fe sulfates. NT2 and the stratigraphically higher samples evolved high-temperature SO₂ peaks (>800 °C) consistent with Mg sulfate (Fig. 2). The Fe and Mg sulfates in the transition samples (BD through AV) either occurred in the amorphous component or were present in low abundances because they were not detected by CheMin [3]. Crystalline Ca sulfate was detected in all 7 samples by CheMin and indirectly detected by the Alpha Particle X-ray Spectrometer (APXS) in many samples throughout Gale crater [3,4]. Ca sulfate by itself thermally decomposes above SAM’s maximum temperature, although its decomposition can be catalyzed by the presence of other phases [5,6]. $\delta^{34}\text{S}$ values calculated from the SO₂ releases were more negative in MG, ZE, AV, and CA than in stratigraphically lower samples (PT, BD, NT).

There are several potential reasons for the $\delta^{34}\text{S}$ variations; for example, they could be due to differences in sulfur sources in the stratigraphically higher samples [7].

The CO_2 evolutions detected by SAM were variable between sample analyses, suggesting C-species heterogeneity within the region as well as within individual drill samples. CA evolved less CO_2 than the stratigraphically lower samples, suggesting less carbonate and/or organics. Evolved CO_2 in the transition samples was consistent with oxidized organic-C, although CO_2 evolved 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. A high-temperature CO release ($\sim 800^\circ\text{C}$) was also observed in the blank, indicating an instrument background source.

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.

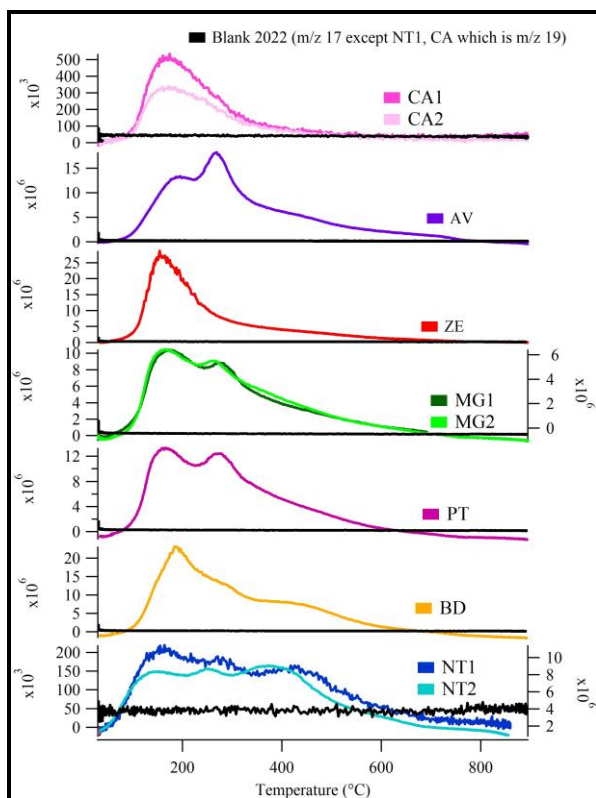


Fig. 1. Evolved H_2O (m/z 17; m/z 19 for NT1, CA1, and CA2) (counts/s) versus temperature from samples drilled in the upper GT, the clay-sulfate transition region, and the base of the sulfate-bearing region.

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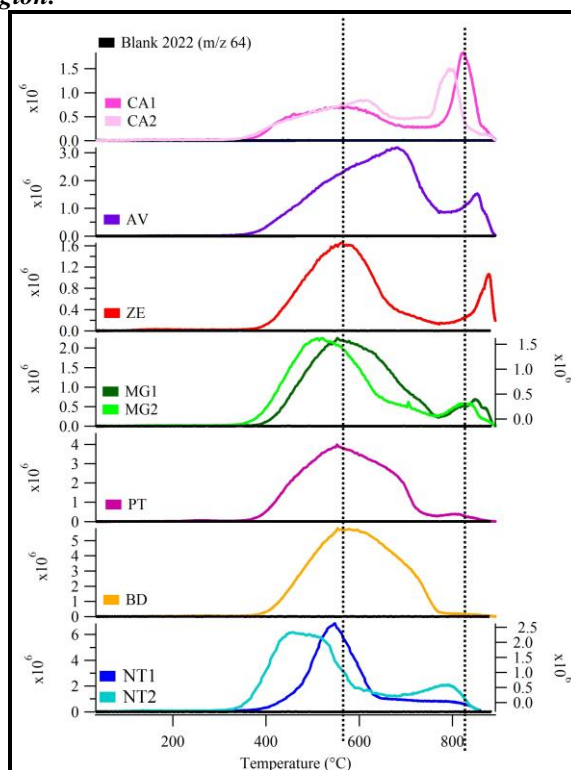


Fig. 2. Evolved SO_2 (m/z 64) (counts/s) versus temperature from samples drilled in the upper GT, the clay-sulfate transition region, and the base of the sulfate-bearing region. Vertical dashed lines represent the approximate peak temperatures of the two major SO_2 releases observed in most samples.

Conclusion: SAM-EGA data collected from samples in and bordering the clay-sulfate transition region were assessed for changes in volatile mineralogy and chemistry. The decrease in mid-temperature H_2O and increase in high-temperature SO_2 in stratigraphically higher samples suggested the disappearance of phyllosilicates and appearance of Mg sulfates, respectively, as the rover approached the sulfate-bearing region. Overall, SAM-EGA data collected from samples in and bordering the clay-sulfate transition region agree with orbital data and suggest that *Curiosity* drove through a region with changing mineralogy. The increasing Mg sulfate and decreasing phyllosilicate abundances, as suggested by SAM-EGA data, support the hypothesis that the clay-sulfate transition region records a major environmental change that may be associated with a key 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. [5] McAdam et al. (2016) 47th LPSC. [6] Knudson et al. (2018) 49th LPSC. [7] Franz et al. (2023) *This LPSC*.