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# Changes in Volatile Mineralogy from the Marker Band Valley to the Layered Sulfate-Bearing Unit in Gale Crater, Mars: Results from the Sample Analysis at Mars-Evolved Gas Analyzer Instrument

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**CHANGES IN VOLATILE MINERALOGY FROM THE MARKER BAND VALLEY TO THE LAYERED SULFATE-BEARING UNIT IN GALE CRATER, MARS: RESULTS FROM THE SAMPLE ANALYSIS AT MARS-EVOLVED GAS ANALYZER INSTRUMENT.** J.V. Clark<sup>1,2</sup>, B. Sutter<sup>2</sup>, A. McAdam<sup>3</sup>, P.D Archer<sup>2</sup>, J. Lewis<sup>3,4,5</sup>, H. Franz<sup>3</sup>, L. Chou<sup>3</sup>, C. Knudson<sup>3,6,7</sup>, J. Eigenbrode<sup>3</sup>, J. Stern<sup>3</sup>, B. Tutolo<sup>8</sup>, L. Hausrath<sup>9</sup>, D. Vaniman<sup>10</sup>, C. Freissinet<sup>11</sup>, D.P. Glavin<sup>3</sup>, A. Steele<sup>12</sup>, C. House<sup>13</sup>, C. Malespin<sup>3</sup>, P. Mahaffy<sup>3</sup>. <sup>1</sup>Geocontrols Systems, Houston, TX, <sup>2</sup>Jacobs JETSII Contract at NASA Johnson Space Center, Houston, TX, <sup>3</sup>NASA Goddard Space Flight Center, Greenbelt, MD, <sup>4</sup>Department of Physics and Astronomy, Howard University, Washington, D.C., <sup>5</sup>Center for Research and Exploration in Space Science and Technology, Greenbelt, MD, <sup>6</sup>University of Maryland, College Park, MD, <sup>7</sup>CRESST II, Greenbelt, MD, <sup>8</sup>The University of Calgary, Calgary, AB, Canada, <sup>9</sup>University of Nevada-Las Vegas, Las Vegas, NV, <sup>10</sup>Planetary Science Institute, Tucson, AZ, <sup>11</sup>LATMOS-IPSL/CNRS, Guyancourt, France, <sup>12</sup>Carnegie Institute for Science, Washington, D.C., <sup>13</sup>Department of Geosciences, The Pennsylvania State University, University Park, PA.

**Introduction:** The *Curiosity* rover traversed a dark-toned, resistant unit in the Amapari member of the Mirador formation, termed the “Marker Band” (MB) that is exposed at multiple locations across Aolis Mons in Gale crater [1]. Sedimentary strata beneath the MB are conformable [1] and include the phyllosilicate-bearing Glen Torridon region [e.g., 2], which transitions into the base of the Layered Sulfate-bearing unit (LSu), interpreted as primarily eolian in origin [3]. The MB is overlain by more LSu, which has orbital spectral data consistent with hydrated Mg sulfates and additional evidence for an eolian origin [e.g., 3, 4]. The MB is comprised of two sedimentological units that have been interpreted as lacustrine: a lower unit with interstratified recessive and resistant beds, and an upper unit with rhythmic laminations [1,5]. The MB and surrounding strata may represent changing geological environments with possible paleoclimate implications. Here, we use Sample Analysis at Mars-Evolved Gas Analysis (SAM-EGA) data to assess mineralogical changes in samples stratigraphically below, within, and above the MB to elucidate differences in mineral formation conditions or geologic processes.

**Methods:** The SAM-EGA instrument analyzed four sedimentary rock drill samples in the lower slopes of the LSu to constrain their volatile chemistry and support mineralogical interpretations made by the Chemistry and Mineralogy (CheMin) X-ray Diffraction (XRD) instrument. Samples, listed in stratigraphic order (lowest to highest), included Canaima (CA), Tapo Caparo (TC), Ubajara (UB), and Sequoia (SQ). All samples, apart from UB, had two subsamples of the same drill material (e.g., CA1 and CA2) because they were further analyzed by gas chromatography after initial SAM-EGA.

CA was sampled from a finely laminated sandstone interpreted as the base of the LSu. TC was drilled in the rhythmically laminated unit of the MB. UB was drilled stratigraphically above the MB with the goal of determining if its mineralogy was in family with previous LSu samples (i.e., CA). SQ was drilled within the LSu in a region with laterally repeating light and

dark-toned “bands” that were observed orbitally and *in-situ* [6]. SQ was drilled in a light-toned band.

All four samples were analyzed by heating samples to ~870 °C (~35 °C/min; 0.8 sccm He carrier gas) [7]. The SAM quadrupole mass spectrometer (QMS) detected evolved gases (e.g., H<sub>2</sub>O, O<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>) at characteristic temperatures consistent with particular phases (e.g., sulfates, carbonates, phyllosilicates).

**Results and Discussion:** CA, TC, UB, and SQ evolved low-temperature (<300 °C) water (Fig.1), which was consistent with adsorbed water, hydrated salts (e.g., gypsum, starkeyite), and hydrated amorphous phases. The broad water releases observed in SQ and TC were consistent with multiple low-temperature water sources including possible akageneite (in SQ) and goethite (in TC).

Mid-temperature (~300-500 °C) water releases were observed in all four samples (Fig.1) and may be attributed to kieserite dehydration or the dehydroxylation of a dioctahedral smectite. CheMin did not detect phyllosilicates in this region and only detected kieserite in TC and SQ [8,9], suggesting that these phases could be below the detection limit of CheMin in CA and UB. Alternatively, amorphous Mg sulfate or amorphous aluminosilicates could be present in these samples.

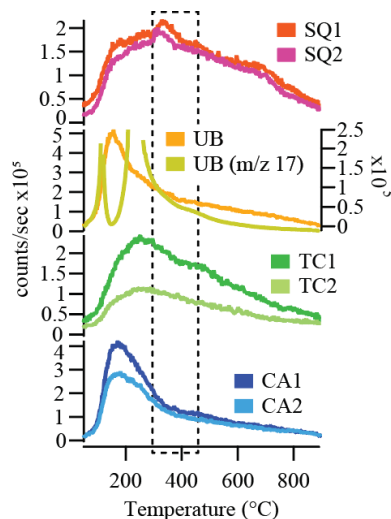
High-temperature (>500 °C) water peaks were not observed in CA, TC, or UB, indicating that phyllosilicates were absent. SQ evolved high-temperature water (~670 °C) consistent with montmorillonite dehydroxylation.

All four samples evolved broad SO<sub>2</sub> releases (peaks ~530 °C) caused by Fe sulfate decomposition (Fig.2). The ~530 °C SO<sub>2</sub> releases were similar between all samples except CA, which evolved SO<sub>2</sub> over a wider temperature range. The CA SO<sub>2</sub> signal could be caused by the presence of poorly crystalline Fe sulfates or catalyzing phases. The ~530 °C SO<sub>2</sub> releases observed in CA-SQ were similar to those observed in clay-sulfate transition samples [10]. Quadratic discriminant analysis (QDA) [11] indicated that no sulfides were present in CA1, TC1, UB, SQ1, and SQ2.

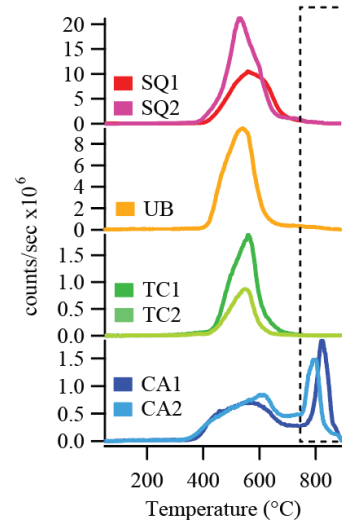
High-temperature (>700 °C) SO<sub>2</sub> releases were not detected in TC, UB, or SQ (Fig.2); this was inconsistent with CheMin's detection of crystalline Mg sulfates [8]. The lack of high-temperature SO<sub>2</sub> in these samples could be due to the limited number of sample phases that catalyze Mg sulfate decomposition (e.g., chlorides) into the SAM temperature range. Alternatively, these samples could contain highly crystalline Mg sulfate, which tend to decompose at a higher temperature than less crystalline varieties [12]. High-temperature SO<sub>2</sub> was observed in CA (Fig.2) and is interpreted as the beginning of starkeyite decomposition. The SO<sub>2</sub> release in CA was similar to samples stratigraphically below CA (uppermost part of the clay-sulfate transition region).

TC, UB, and SQ evolved CO<sub>2</sub> with peaks ~400 °C, consistent with laboratory runs of siderite [13] (data not shown). This supported CheMin's detection of siderite in TC, UB, and SQ [9]. Stratigraphically lower samples with this distinct CO<sub>2</sub> release may have contained siderite below CheMin's detection limit.

Oxychlorines and nitrates were not present in any of the four samples due to the non-detection of O<sub>2</sub> and NO (data not shown). Oxychlorines and nitrates were possibly not deposited in these sediments or they were removed by leaching. Broad HCl releases (peaks ~600 °C) were observed in all four samples and suggested the presence of chlorides, similar to stratigraphically lower samples. UB evolved an additional HCl peak at ~350 °C that could be caused by MgCl<sub>2</sub>.



**Fig. 1.** Evolved H<sub>2</sub>O (m/z 20) from samples drilled in the lower LSU and MB. Samples are ordered stratigraphically, with the lowest sample on the bottom. m/z 17 is shown for UB to highlight the mid-temperature H<sub>2</sub>O release, although the detector was saturated at lower temperatures. The dashed box represents H<sub>2</sub>O from kieserite dehydration.



**Fig. 2.** Evolved SO<sub>2</sub> (m/z 64 or 66) from samples drilled in the lower LSU and MB. Samples are ordered stratigraphically. Dashed box represents SO<sub>2</sub> attributed to Mg sulfates.

**Conclusions:** SAM-EGA data suggest that the MB and overlying LSU strata are distinct from underlying rocks in terms of their evolved volatiles. One major change in this region was the detection of CO<sub>2</sub> from siderite decomposition in the MB and overlying samples, which could indicate neutral to alkaline and anoxic formation waters. The non-detection of SO<sub>2</sub> above 700 °C in TC, UB, and SQ was potentially inconsistent with CheMin's detection of Mg sulfates in several samples, though this may be due to factors such as Mg sulfate crystallinity or absence of catalyzing minerals. Water releases were consistent with hydrated salts (e.g., starkeyite) and kieserite dehydration. SAM-EGA data from the MB were not drastically different from overlying samples in the LSU, suggesting that secondary mineral formation waters may have been chemically similar and other factors should be considered for impacting the induration of the MB. Factors to consider include differences in grain size and/or porosity/permeability, which may have resulted from differences in depositional environment (lacustrine in the MB and eolian in overlying strata[3]).

[1] Gupta et al. (2023) *LPSC*, The Woodlands, TX. [2] McAdam et al. (2021) *JGR Plan.*, 127. [3] Edgar et al. (This LPSC). [4] Milliken et al. (2010) *GRL*, 37. [5] Weitz et al. (2023) *LPSC*, The Woodlands, TX. [6] Roberts et al. (2023) *LPSC*, The Woodlands, TX. [7] Mahaffy et al. (2012). *Spa. Sci. Rev.*, 170. [8] Vaniman et al. (This LPSC). [9] Tutolo et al. (This LPSC). [10] Clark et al. (2023) *LPSC*, The Woodlands, TX. [11] Wong et al. (2020) *JGR Plan.*, 125. [12] Clark et al. (2023b) *LPSC*, The Woodlands, TX. [13] Archer et al. (2020) *LPSC*, The Woodlands, TX.