

CONSTRAINTS ON THE CHEMISTRY AND MINERALOGY OF THE CLAY-BEARING UNIT FROM SAMPLE ANALYSIS AT MARS EVOLVED GAS ANALYSES. A. C. McAdam¹, B. Sutter², P. D. Archer², H. B. Franz¹, J. L. Eigenbrode¹, J. C. Stern¹, C. A. Knudson^{1,3}, J. M. T. Lewis¹, G. M. Wong⁴, S. Andrejkovičová^{1,3}, J. V. Hogancamp^{2,5}, C. N. Achilles¹, D. W. Ming⁶, R. V. Morris⁶, T. F. Bristow⁷, E. B. Rampe⁶, R. Navarro-Gonzalez⁸, S. S. Johnson⁹, A. J. Williams¹⁰, and P. R. Mahaffy¹, ¹NASA/GSFC, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, ²Jacobs, NASA/JSC, ³CRESST, Univ. of Maryland, ⁴Pennsylvania State Univ., ⁵Geocontrols Systems Inc, ⁶NASA/JSC, ⁷NASA/ARC, ⁸Univ. Nacional Autónoma de México, ⁹Georgetown Univ., ¹⁰Univ. of Florida.

Introduction: The clay-bearing unit (CBU), also termed Glen Torridon (GT), has long been a priority target for the Mars Science Laboratory (MSL) mission because of spectral signatures of smectite identified in these Mt. Sharp strata from orbit by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM). These minerals can be key indicators of habitable environments [1,2] and possibly facilitate the preservation of organic compounds [3-6]. The CBU is overlain by sulfate-bearing layers and this sequence may record a large-scale change in aqueous conditions with time [7]; probing the textural, geochemical and mineralogical signatures of that change are another driver for the priority placed on exploring this area. MSL recently drilled the Murray Formation (Fm.) mudstone of GT in an area where smectite detections by CRISM are strongest and which is the lowest elevation part of the CBU along the planned rover path. This area near an eroding scarp of the Vera Rubin ridge (VRR) could have a relatively young exposure age, potentially making it well suited to the search for preserved organic compounds.

Textural and chemical analyses to date are overall consistent with the rocks of GT being similar to previously observed Murray formation rocks but within that existing range of Murray chemistry there seem to be two distinct bedrock compositions present at GT [8,9]. One is a coherent bedrock which is relatively high in Mg and low in K. The other is a rubbly bedrock which is relatively low in Mg and high in K. Chemistry and Mineralogy (CheMin) instrument analyses of drill samples in GT, from targets Aberlady (AL) and Kilmorie (KM) on a block of coherent bedrock material, showed significant abundances of smectite clay minerals and relatively low amounts of hematite [10].

The Sample Analysis at Mars (SAM) instrument suite on MSL has been essential in understanding volatile-bearing phases in Gale Crater materials. SAM's evolved gas analysis mass spectrometry (EGA-MS) has detected H₂O, CO₂, O₂, H₂, SO₂, H₂S, HCl, NO, and other trace gases, including organic fragments, in many samples. The identity and evolution temperature of evolved gases can support CheMin instrument X-ray diffraction (XRD) mineral detection and place constraints on trace volatile-bearing phases or phases difficult to characterize with XRD (e.g., amorphous phases). At the time of this writing, SAM has just performed its

first EGA-MS analysis of a GT sample, KM, and interpretation of the data is ongoing. We anticipate several additional analyses of GT drill samples in the near term. Here we discuss several preliminary interpretations of EGA-MS data from KM and some considerations based on analyses of prior samples of Murray formation rocks, with an example from the lower Murray (Mojave, MJ), upper Murray (Marimba, MB), Murray of the Blunt's Point member directly beneath the resistant members of the VRR (Duluth, DU) and a sample of the Jura member in the VRR (Rock Hall, RH).

Methods: During EGA-MS analyses, sample fines are heated to ~860°C at 35°C/min. Evolved gases are carried by an He carrier gas (~0.8 sccm, 25 mb in the pyrolysis oven) to the MS where they are detected by the mass-to-charge ratio (m/z) of the molecule or an isotopologue or MS fragment of the molecule (e.g., H₂O is represented by m/z 17, 18 or 20).

Considerations for SAM EGA results at GT: *Phyllosilicates:* Though previous areas stratigraphically below the GT did not display the strong orbital spectral signatures of phyllosilicates, phyllosilicates dominated by smectite clay minerals were detected below GT by SAM and CheMin. These smectites in the Murray trend from trioctahedral to dioctahedral, and more Al and Fe³⁺, with increasing elevation consistent with increasing oxidation and element mobility in generally more open system environments [10,11]. In SAM data, this trend can be seen in changes in H₂O evolution peak temperature due to smectite dehydroxylation at pyrolysis temperatures above ~450°C, with dioctahedral smectites dehydroxylating at lower temperature than trioctahedral [12,13] (Fig. 1a and 1b).

Differences in clay mineral composition are a possible explanation for differences in the Mg and K content of the two major bedrock constituents of GT analyzed by ChemCam [8] and Alpha Particle X-ray Spectrometer (APXS) [9]. SAM EGA H₂O data can enable the distinction between several different types of phyllosilicates (several examples in Fig. 1b). The H₂O data from KM is still being interpreted, but water evolution between ~400-600°C is consistent with dehydroxylation of Fe-rich dioctahedral smectites in the sample. Water evolution at lower temperatures likely derives from the X-ray amorphous component of the sample. Subtle H₂O evolution near 715°C is still being evaluated.

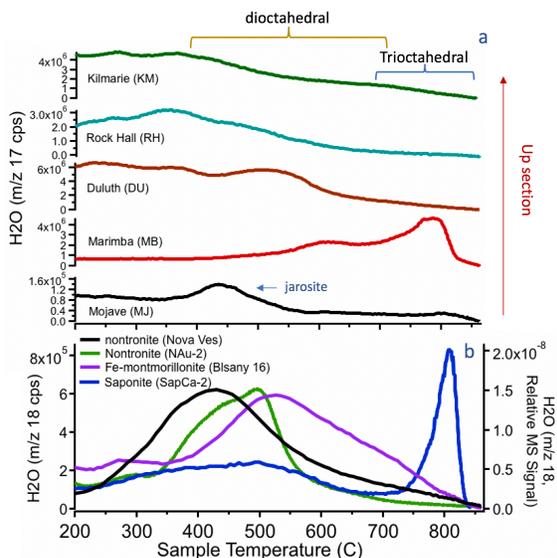


Figure 1. a) SAM H₂O EGA data from selected Murray Fm. samples with increasing elevation. b) EGA data from SAM-like lab runs of selected smectites.

Sulfur-bearing minerals: Evolved SO₂ is attributed to Fe sulfate or sulfide and Mg sulfate minerals that occur at abundances below CheMin detection limits and/or are X-ray amorphous. All samples to date have contained X-ray amorphous material, and many Mg and Fe sulfates can be amorphous under Mars conditions [14,15]. The SO₂ evolution temperatures can be used to distinguish Fe sulfate and sulfide from Mg sulfate evolution, with the former evolving SO₂ from ~500-700°C and the latter >700°C (Fig. 2). KM exhibited SO₂ consistent with both Fe sulfates/sulfides and Mg sulfates. Ca sulfate will not decompose in the SAM temperature range. SO₂ evolutions consistent with Fe sulfate can be indicators of acidic depositional or diagenetic conditions.

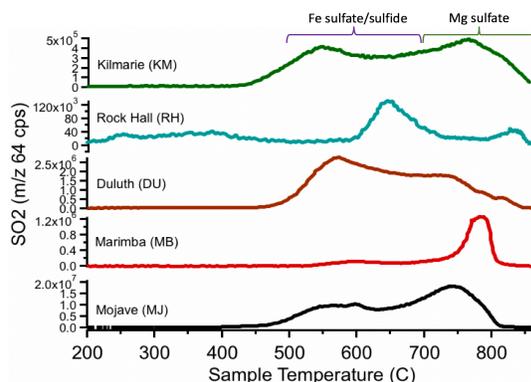


Figure 2. SAM SO₂ EGA data from selected Murray Formation samples.

Oxidized carbon phases: CO₂ evolutions observed above ~500°C are consistent with thermal

decomposition of a carbonate mineral. CO₂ and CO evolution at lower temperatures, observed in KM, and several samples to date, are usually attributed to organic salts such as oxalates with possible minor contributions from oxidation of reduced C by evolved O₂ in some samples.

Oxychlorine and nitrate salts: Starting with samples of the Upper Murray, evolved O₂ was no longer observed in SAM analyses and NO was absent or very minor. One possible explanation was that post-depositional processes leached initially deposited soluble oxychlorine and nitrates. Alternatively, unlike samples below the Upper Murray, oxychlorine and nitrate were never deposited. The VRR RH sample, however, evolved O₂ and NO, attributed to a reoccurrence of oxychlorine and nitrate minerals. At KM, no O₂ evolution was observed, and very little NO, implying no oxychlorine and little nitrate salts. The presence of these salts in some Murray mudstones of the VRR (at RH) and their absence or near absence in nearby VRR and GT Murray as represented by KM, can place constraints on the diversity of diagenetic fluids that have affected different parts of the Murray. Data to date indicate that Murray mudstones record a complex depositional and diagenetic history.

Summary: Overall, constraints on the nature, composition and potential provenance of GT materials enabled by SAM EGA data, in the context of other mineralogical, geochemical, and geomorphological information obtained by the rover, will inform the depositional and diagenetic history preserved in the clay-bearing unit and contribute to assessment of Gale crater's environmental history, past habitability, and organic preservation potential. In addition, depending on the results of SAM EGA analyses, and pyrolysis gas chromatography mass spectrometry (GCMS) analyses, one or more of SAM's wet chemistry experiments could be utilized in GT. These experiments can facilitate the detection of some organic compounds through reactions with liquid derivatization or thermochemolysis agents that can make some organics more volatile and therefore detectable by GCMS [e.g., 6,16].

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