

INVESTIGATION OF THE GLEN TORRIDON CLAY-BEARING UNIT AND OVERLYING GREENHEUGH PEDIMENT BY THE SAMPLE ANALYSIS AT MARS INSTRUMENT SUITE. A. C. McAdam¹, B. Sutter², P. D. Archer², H. B. Franz¹, J. L. Eigenbrode¹, C. A. Knudson^{1,3}, J. M. T. Lewis^{1,4}, G. M. Wong⁵, J. V. Clark^{2,6}, M. Millan^{1,7}, A. J. Williams⁸, S. Andrejkovičová^{1,3,9}, C. Freissinet¹⁰, D. P. Glavin¹, J. C. Stern¹, R. Navarro-González¹¹, C. N. Achilles¹, D. W. Ming¹², R. V. Morris¹², T. F. Bristow¹³, E. B. Rampe¹², M. T. Thorpe¹², A. S. Yen¹⁴, C. H. House⁵, A. B. Bryk¹⁵, V. K. Fox¹⁶, K. A. Bennett¹⁷, S. S. Johnson⁷, P. R. Mahaffy¹, and C. A. Malespin¹, ¹NASA Goddard Space Flight Center (Amy.McAdam@nasa.gov), ²Jacobs, NASA JSC, ³CRESST/Univ. of Maryland, College Park, ⁴CRESST/Howard Univ., ⁵Pennsylvania State Univ., ⁶Jacobs JETS Contract, ⁷Georgetown Univ., ⁸Univ. of Florida, ⁹Aveiro Univ., ¹⁰LATMOS-IPSL/CNRS/UVSQ, ¹¹Univ. Nacional Autonoma de Mexico, ¹²NASA JSC, ¹³NASA ARC, ¹⁴JPL/Caltech, ¹⁵Univ. of California, Berkeley, ¹⁶Univ. of Minnesota, ¹⁷USGS Astrogeology Science Center.

Introduction: Exploring the Glen Torridon (GT) clay-bearing unit in Gale crater has long been a prime goal for the Mars Science Laboratory (MSL) because of spectral signatures of smectite identified from orbit. Smectite clay minerals can indicate habitable environments [1,2] and possibly facilitate the preservation of organic compounds [e.g., 3-7]. Also, sulfate-bearing layers overlie GT and this sequence may record a large-scale change in aqueous conditions over time [8].

The Sample Analysis at Mars (SAM) instrument suite has been essential in understanding volatile-bearing phases in Gale crater materials. SAM EGA has detected H₂O, CO₂, O₂, H₂, SO₂, H₂S, HCl, NO, and other trace gases, including organic fragments, evolved from many samples on heating. The identity and evolution temperature of evolved gases can support mineral detection by CheMin instrument X-ray diffraction (XRD) and place constraints on trace volatile-bearing phases, clay mineral compositions, and X-ray amorphous materials.

In GT, SAM analyzed the sample Kilmorie (KM) from the Jura member, Glen Etive (GE), Mary Anning (MA) and Groken (GR) from the Knockfarril Hill member (KHm), Glasgow (GG) and Hutton (HU) from the fractured Intermediate Unit (fIU), and Edinburgh (EB) from the Stimson formation rocks of the Greenheugh Pediment (GP). The Jura, KHm and fIU are all members of the Murray formation. HU was sampled near the basal Siccar Point group (SPg) unconformity between the fIU and GP, in an area that exhibits a brighter tone and differences in geochemistry compared to Murray materials down-section [9,10]. CheMin XRD of most samples (except for HU and EB) showed large abundances of smectite clay minerals (~25-35%) and all samples showed X-ray amorphous materials and relatively low amounts of well-crystalline hematite [11]. SAM evaluated mineralogy through evolved gas analysis mass spectrometry (EGA) while detailed organic chemistry of several samples was examined by pyrolysis gas chromatography mass spectrometry and wet chemistry experiments [12,13]. Here we discuss data and interpretations from SAM EGA analyses.

Methods: During SAM EGA, 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) to the mass spectrometer (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.

Results: *Phyllosilicates and other H₂O-evolving phases:* All samples exhibited ~2 peaks below 300°C, superimposed on a wide evolution (peaks 1 and 2, Fig. 1). These peaks are thought to result from adsorbed water, hydrated salts, and hydrated/hydroxylated X-ray amorphous phases. H₂O evolved from ~350-550°C from all samples is consistent with dehydroxylation of a Fe-rich dioctahedral smectite, such as nontronite (peak 3 region, Fig. 1). In HU, very little water evolved in that temperature range indicates less smectite than the other samples, possibly due to alteration of pre-existing smectite during aqueous events near the SPg unconformity.

H₂O evolution >600°C in several samples (peak 4 region, Fig. 1) is attributed to dehydroxylation of additional trace phyllosilicates (for example, mixed layer Fe-talc/serpentine possibly indicated by CheMin analyses of some samples [11] is expected to evolve H₂O in this temperature range).

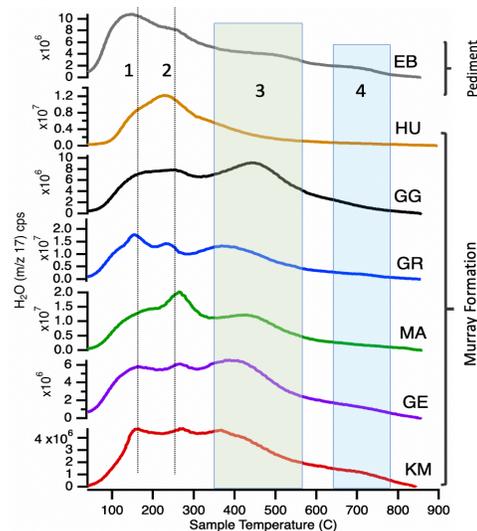


Fig 1. SAM H₂O EGA data from GT and GP samples.

Salts: SO₂ evolved from ~450-700°C was attributed to Fe sulfate or sulfide and SO₂ evolved >~700°C was attributed to Mg sulfate. These occur at trace abundances and/or are X-ray amorphous because they were not detected by XRD. Ca sulfate detected by XRD will not decompose in the SAM temperature range. KM, GE, GR and EB SO₂ is consistent with Fe sulfates/sulfides and Mg sulfates, while MA, GG, and HU show primarily SO₂ consistent with Fe sulfates/sulfides.

No O₂, and very little NO, evolution was observed except for in EB EGA, implying no oxychlorine and little nitrate salts in all samples except EB. A lack of evolved O₂ also indicates that, even in Mn-rich samples such as GR [14,15], it is unlikely that Mn^{3+/4+} oxides are present because many of those evolve O₂ in the SAM temperature range [16]. If present, Mn oxides are likely Mn²⁺ [16]. All samples evolved HCl as a wide evolution from 300 to ~850°C, except that KM exhibited only a low HCl evolution and GR's HCl trace was dominated by a peak at ~780°C. HCl evolutions likely derive from interaction of trace chloride salts (undetected by ChemMin) with evolved H₂O or other materials during heating. In the case of GR, the peak at ~780°C is consistent with chlorides such as NaCl or MnCl₂ [16].

Carbon phases: CO₂ evolution from GT samples indicates C contents from ~400 to 2800 ugC/g. The temperatures of CO₂ evolution from all the samples are consistent with oxidized organic carbon (e.g., oxalate salts) but CO₂ evolved above 360°C could have contributions from carbonate decomposition [17]. ChemMin detected siderite in KM and GE, and possibly in MA and GR [11]. CO is usually co-evolved with CO₂ indicating that some CO₂ derives from oxidized organics (carbonate does not evolve CO). The abundances of CO are usually much less than CO₂, except in the case of GG; this may indicate that GG contains more oxidized organics [18].

Discussion and Conclusions: Mineral and chemical constraints from EGA enable several insights into aqueous interactions experienced by GT and GP rocks.

Chemistry of fluids: EGA data consistent with smectites being the dominant phyllosilicate, and the presence of siderite in several samples, suggest instances of neutral/alkaline fluid interactions. Likely Fe sulfates in all samples, however, suggests at least some localized interactions with acidic fluids. Variations in Fe and Mg sulfate distributions from KM to HU are consistent with changes in fluid chemistry up section in the Murray from the Jura to the flU.

Redox characteristics: Siderite in some samples, and the possibility of Mn²⁺ oxides in some samples such as GR, suggest reducing conditions during some fluid interactions. Conversely, the presence of significant abundances of ferric iron rich smectites and oxidized carbon compounds (carbonates, partially to fully

oxidized organic compounds) in all samples indicates episodes of oxidizing conditions.

Water-to-rock ratios (W/R): The Fe-rich dioctahedral smectites (e.g., nontronites) indicated by H₂O EGA data, the lack of highly soluble oxychlorine salts, and the very trace abundances of very soluble nitrate salts, suggest generally higher W/R alteration episodes compared to those recorded in smectite-bearing rocks encountered earlier in the mission. Yet, HCl EGA data point to soluble chlorides in all samples suggesting that not all aqueous alteration episodes were high W/R.

Nature of processes along the SPg unconformity: Differences between the salt contents of the EB sample (oxychlorine, nitrate and Mg sulfate salts present) and underlying HU and GG Murray samples (no oxychlorine, nitrate or Mg sulfate salts) suggest that groundwater did not infiltrate through the pediment and carry salts into the underlying sediments. In addition, EGA indicated differences in carbon and clay mineral phases and abundances between EB and underlying Murray [19]. These observations are consistent with diagenetic alteration during fluid flow along the contact and/or subaerial alteration before pediment emplacement [19].

Oxychlorine and nitrate salts at EB record at least one episode of interaction with a brine of different composition than the alteration fluids indicated by GT Murray mineralogy. It may be that similar brines never interacted with GT Murray rocks, or that the perchlorate and nitrate records of such interactions in GT Murray were erased by later leaching. In the case of a leaching event, deposition of soluble chlorides in the GT Murray must have occurred after this event or leaching occurred under conditions that allowed chlorides to remain.

Overall, SAM's EGA results indicate that GT and GP rocks have likely experienced a complex depositional and diagenetic history involving aqueous alteration episodes with fluids of varying pH, chemical composition, and redox characteristics and with variable fluid-to-rock ratios. The indicated episodes could have provided habitable environmental conditions.

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