

**CONSTRAINTS ON THE MINERALOGY OF MUDSTONES FROM THE VERA RUBIN RIDGE, GALE CRATER, MARS, FROM EVOLVED GAS ANALYSES.** A. C. McAdam<sup>1</sup>, B. Sutter<sup>2,3</sup>, P. D. Archer<sup>2,3</sup>, H. B. Franz<sup>1</sup>, J. L. Eigenbrode<sup>1</sup>, J. C. Stern<sup>1</sup>, G. M. Wong<sup>4</sup>, J. M. T. Lewis<sup>1</sup>, C. A. Knudson<sup>1,5</sup>, S. Andrejkovicova<sup>1,5</sup>, J. V. Hogancamp<sup>2,3,6</sup>, C. N. Achilles<sup>1</sup>, D. W. Ming<sup>3</sup>, R. V. Morris<sup>3</sup>, E. B. Rampe<sup>3</sup>, T. F. Bristow<sup>7</sup>, R. Navarro-Gonzalez<sup>8</sup>, S. S. Johnson<sup>9</sup>, and P. R. Mahaffy<sup>1</sup>, <sup>1</sup>NASA/GSFC, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, <sup>2</sup>Jacobs, <sup>3</sup>NASA/JSC, <sup>4</sup>Pennsylvania State Univ., <sup>5</sup>CRESST, Univ. of Maryland, <sup>6</sup>Geocontrols Systems Inc, <sup>7</sup>NASA/ARC, <sup>8</sup>Univ. Nacional Autónoma de México, <sup>9</sup>Georgetown Univ.

**Introduction:** The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) rover has been essential in understanding volatile-bearing phases in Gale Crater materials. SAM's evolved gas analysis mass spectrometry (EGA-MS) has detected H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, 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). For the past ~500 sols, MSL has been exploring the Vera Rubin Ridge (VRR), which exhibits a striking hematite signature in orbital remote sensing data [1], to understand the depositional and diagenetic history recorded in the Murray mudstones of the VRR and how it relates to the underlying Murray. One rock sample was drilled from the Blunts Point Member (Duluth, DU), which is stratigraphically directly beneath the resistant members of the VRR and three rock samples were drilled from the VRR, one from the Pettegrove Point Member (Stoer, ST), and two from the Jura Member - one gray endmember (Highfield, HF) and one red endmember (Rock Hall, RH). The Jura displays differences in color, and a key goal was to constrain the cause of this color difference and the associated implications for depositional or post-depositional conditions. Here we present an overview of results from SAM EGA-MS analyses of VRR materials with some comparisons to prior analyses.

**Methods:** For SAM EGA-MS analyses, sample fines were heated to ~860°C at 35°C/min. The DU sample was 4x larger in delivered volume than ST and HF; the DU EGA signals in Fig. 1 are divided by 4 for straightforward comparison to ST and HF. Evolved gases were carried by an He carrier gas (~0.8 sccm, 25 mb in the pyrolysis oven) to the MS where they were detected by the mass-to-charge ratio (m/z) of the molecule or an isotopologue or MS fragment of the molecule (e.g., H<sub>2</sub>O is represented by m/z 17, 18 or 20).

**Results and Discussion:** Water was released from all samples, in similar abundances to previous Murray Formation samples (~1-2 wt%) [2]. In general, all samples evolved water as a wide release between ~100-600°C, but traces exhibited interesting differences in peaks superimposed on a broad evolution (Figure 1a).

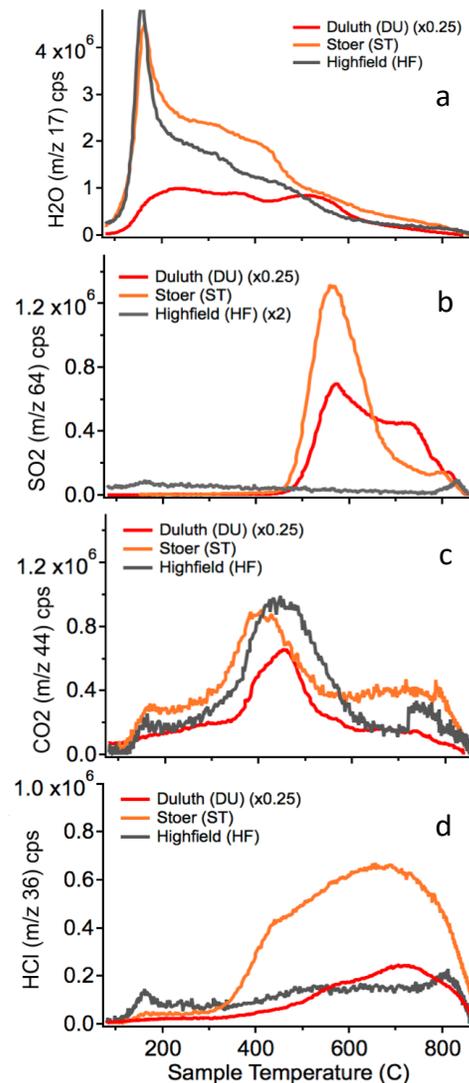


Fig 1. SAM EGA-MS data from Duluth (DU), Stoer (ST), and Highfield (HF) for a) H<sub>2</sub>O, b) SO<sub>2</sub>, c) CO<sub>2</sub>, and d) HCl.

Evolved water traces indicated the presence of hydrated Ca sulfates (gypsum, bassanite), phyllosilicates, and possibly akaganeite and jarosite. ST and HF traces have sharp peaks at ~150°C which likely result from dehydration of hydrated Ca sulfates [3]. Small peaks superimposed on the broader evolution near ~250-300°C could result from trace or tentatively detected akaganeite detected by CheMin, or possibly similar phases present below the CheMin detection limits. The peaks

superimposed on the broad evolution between about 400 and 600°C are likely from H<sub>2</sub>O evolved during dehydroxylation of the dioctahedral smectite present in samples [3]. The temperature of this peak can help constrain the Fe composition of the smectite's octahedral layer, with lower temperatures indicating more Fe. These peak temperatures for all the samples are consistent with an Fe-rich dioctahedral smectite. The trend in the peak temperatures implies that smectites in ST and HF have more Fe than those in DU. In ST, some H<sub>2</sub>O near ~450°C can also result from dehydroxylation of trace jarosite in this sample [3]. The amorphous component in all samples can also contribute some H<sub>2</sub>O.

DU and ST evolved similar total amounts of SO<sub>2</sub> (~1 wt.% SO<sub>3</sub>) and their EGA-MS traces show the most evolution near 600°C, and lesser evolutions between 700 and 800°C (Figure 1b). HF, however, evolved a lesser amount of SO<sub>2</sub> (~0.1 wt.% SO<sub>3</sub>) and most SO<sub>2</sub> was evolved at very high temperature with a peak at ~800°C. A smaller peak was also seen below 200°C.

Evolved SO<sub>2</sub> releases were consistent with Fe sulfate/sulfide and/or Mg sulfate. The peaks near 600°C are consistent with SO<sub>2</sub> evolution from Fe sulfates and/or Fe sulfides. The peaks in the 700-800°C range are consistent with Mg sulfate decomposition. No crystalline Fe or Mg sulfates were detected by CheMin (except for trace jarosite in ST), indicating that these sulfates inferred by SAM data are likely part of the x-ray amorphous material and/or trace S phases present below CheMin's detection limit. Mg and Fe sulfates are likely to be amorphous under many martian conditions [4].

DU, ST and HF all evolved similar amounts of C as CO<sub>2</sub> (~0.1-0.4 wt.% CO<sub>2</sub>). The CO<sub>2</sub> EGA-MS traces from DU, ST and HF look generally similar, with most CO<sub>2</sub> evolved between ~300-600°C with peak temperatures less than ~500°C (Figure 1c). The CO<sub>2</sub> evolutions are consistent with organic C from oxidized C phases such as oxalates and acetates [e.g., 2]. Combustion of organic C to CO<sub>2</sub> is unlikely because no O<sub>2</sub> evolved from these samples. CO<sub>2</sub> from carbonate decomposition would be expected above 450-500°C and could contribute some of the CO<sub>2</sub> if it was present at abundances below CheMin detection limits. The samples also evolved CO between 300-600°C, supporting the inference of organic salts such as oxalates in the samples.

No O<sub>2</sub> was evolved from the VRR samples to date, indicating either a lack of oxychlorine phases (e.g., perchlorates, chlorates) in these samples or scrubbing of any oxygen evolved during heating by other materials in the samples [5,6]. There was also very little or no NO evolved from these samples, implying a lack of nitrate salts. Upper Murray samples stratigraphically below the VRR also exhibited low amounts or non-detections of evolved O<sub>2</sub> and NO. An absence of these soluble salts

may imply post-depositional leaching, or that these salts were not present in the original depositional environment [5,6]. There are various features in the VRR which suggest several post-depositional fluid events [e.g., 7,8]; these may have served to mobilize soluble oxychlorine and nitrate minerals (as well as other phases).

HCl EGA-MS traces from ST and DU look similar overall, with a wide evolution starting at 300-400°C and continuing until approximately the end of the temperature range (Figure 1d). HF's HCl trace looks different; with the major features being subtle peaks <200°C and at 800°C. HCl can be from reactions between trace chlorides and water evolved from the sample during heating (e.g., water evolved from salts or phyllosilicates). Trace akaganeite detected in ST by CheMin [3] could also contribute HCl.

At the time of this writing, SAM is preparing to analyze the final sample of the VRR, Rock Hall. We plan to also report on the results of this analysis and comparison to the other VRR samples.

**Implications:** SAMEGA H<sub>2</sub>O data indicating iron-rich dioctahedral smectites has been rare to date. These smectites can be consistent with oxidation and elemental mobilization, and possibly acidic or mildly acidic fluid interactions. In DU and ST, SO<sub>2</sub> evolution consistent with Fe sulfate is also observed; these sulfates may be indicative of acidic interactions.

The potential reasons for the lack of oxychlorine and nitrate minerals in the VRR samples are still being explored. It is consistent with a leaching environment that could have favored the formation of dioctahedral smectites, though if that occurred other, possibly soluble, chlorine minerals (e.g., trace chlorides) persisted, based on EGA HCl evolutions (and APXS Cl measurements). These characteristics likely derive from a complex history of post-depositional aqueous alteration under a range of geochemical conditions, an idea that is consistent with other lines of evidence [e.g., 7,8,9] that VRR rocks have probably experienced several different episodes of post-depositional fluid-rock interactions.

Overall, constraints on the nature and composition of VRR materials enabled by SAM EGA data, in the context of other mineralogical, geochemical, and stratigraphic information obtained by the rover, inform hypotheses about the depositional and diagenetic history recorded in the rocks of the VRR.

**References:** [1] Fraeman, A. A., et al. (2018) *LPSC*, 49, #1557. [2] Sutter, B., et al. (2017) *JGR-Planets*, 122, 2574. [3] Morris, R. V., et al. (2019) *LPSC*, 50. [4] Vaniman, D. T., et al. (2004) *Nature*, 431, 663. [5] Archer, P. D., et al. (2019) *LPSC*, 50. [6] Sutter, B., et al., (2019) *LPSC*, 50. [7] Sun, V. Z., et al. (2019) *Icarus*, 321, 866. [8] Haridon, J., et al. (2018) Fall AGU, P41A-07. [9] Thompson, L. M., et al. (2019) *LPSC*, 50.