

**EVOLVED GAS ANALYSES OF MUDSTONES FROM THE VERA RUBIN RIDGE.** 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>, P. R. Mahaffy<sup>1</sup> <sup>1</sup>NASA Goddard Space Flight Center, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, <sup>2</sup>Jacobs, Houston, TX 77058, <sup>3</sup>NASA/JSC, Houston, TX 77058, <sup>4</sup>Pennsylvania State Univ., University Park, PA 16802, <sup>5</sup>CRESST, Univ. of Maryland, College Park, MD, 20742, <sup>6</sup>Geocontrols Systems Inc, Houston, TX, <sup>7</sup>NASA Ames Research Center, Moffett Field, CA, 94035, <sup>8</sup>Univ. Nacional Autónoma de México, México, D.F. 04510.

**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 mineral detection and place constraints on trace volatile-bearing phases or phases difficult to characterize with X-ray diffraction (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], in order to understand the depositional and diagenetic history recorded in the rocks and how it relates to the underlying Murray Formation. Four rock samples were drilled, one from the Blunts Point Member (Duluth, DU), one from the Pettegrovve Point Member (Stoer, ST), and two from the Jura Member. The Jura Member displays differences in color, summarized as grey and red, and a key goal was to constrain the cause of this color difference and the associated implications for depositional or post-depositional conditions. To investigate, a grey (Highfield, HF) and a red (Rock Hall, RH) Jura sample were drilled. Here we will give an overview of results from SAM EGA-MS analyses of VRR materials, with some comparisons to analyses of samples of the underlying Murray.

**Methods:** For SAM EGA-MS analyses, sample fines were heated to ~860°C at 35°C/min. Duluth was the first sample drilled with a new method, so DU and the subsequent ST, HF and RH samples were delivered with a different processing and portioning method than used previously. A consequence of this new method is that there is more uncertainty in the mass of sample delivered, but abundances of minerals detected in CheMin analyses that also evolve gases during SAM analyses (e.g., hydrated salts, phyllosilicates) can be used to estimate the mass of sample that was delivered to SAM.

Evolved gases were carried by an He carrier gas 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). The pressure of He in the oven was

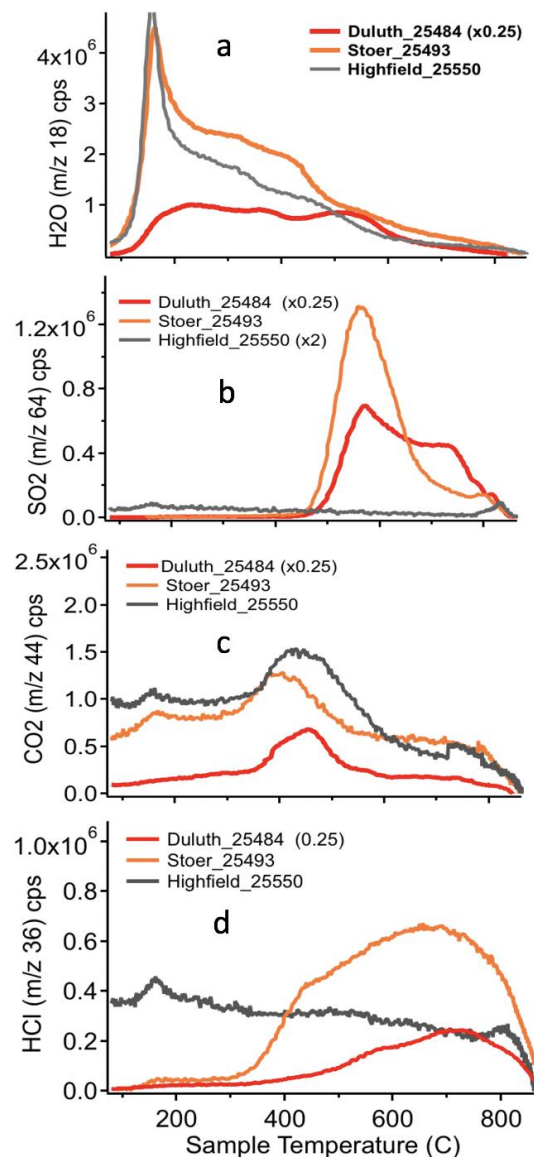


Fig 1. SAM EGA-MS data from Duluth, Stoer, and Highfield for a) H<sub>2</sub>O, b) SO<sub>2</sub>, c) CO<sub>2</sub>, and d) HCl. [Will fix c and d background subtraction]

~25 mb and the flow rate was ~0.8 standard cubic centimeters per minute.

**Results and Discussion:** H<sub>2</sub>O was released from all samples, in similar abundances to previously analyses of Murray Formation samples (~1-2 wt%) [3]. In

general, all samples evolved water as a wide release between about 100-600 C, but traces exhibited interesting differences in peaks superimposed on a broad evolution (Figure 1a). ST and HF traces have sharp peaks at ~150 C which likely result from dehydration of the significant hydrated Ca sulfates detected in these samples by CheMin [1]. Small peaks superimposed on the broader evolution near ~300 C in all samples 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 at high temperature are likely from H<sub>2</sub>O evolved during dehydroxylation of the dioctahedral smectite present in samples at ~4-10 wt. % [1]. The temperature of this peak can give constraints on 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 [1]. 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> and their EGA-MS traces show the most evolution near 600 C, and lesser evolutions near 700 C (Figure 1b). HF, however, evolved a lesser amount of SO<sub>2</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 <200 C. The peaks near 600 C are consistent with thermal decomposition of Fe sulfates. The peaks in the 700-800 C range are consistent with Mg sulfate decomposition. No crystalline Fe or Mg sulfates were clearly detected by CheMin (except for possible trace jarosite in ST), indicating that these sulfates inferred by SAM data are likely part of the x-ray amorphous components of the samples and/or trace S phases present near or below CheMin's detection limit. Mg and Fe sulfates are likely to be amorphous under many martian conditions [2].

DU, ST and HF all evolved similar amounts of C as 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., 3]. Combustion of organic carbon to CO<sub>2</sub> is unlikely because of a lack of 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> observed. The samples also evolved CO between 300-600 C, supporting the inference of organic salts such as oxalates in these samples.

No O<sub>2</sub> was evolved from the VRR samples, 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 [4,5]. There was also very little or no NO evolved from these samples, implying a lack of nitrate salts. Upper Murray samples below 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 [4,5]. There are various features in the VRR which suggest several post-depositional fluid events [6,7]; 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; there are no wide evolutions only 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 some samples by CheMin [1] 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:** SAM EGA-MS data from VRR samples indicates that sample smectites detected by CheMin [1] are likely iron-rich dioctahedral smectites, with some variation in the octahedral iron content. SAM EGA 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 can be indicative of acidic interactions.

The potential reasons for the lack of O<sub>2</sub> and NO evolved from VRR samples (and Upper Murray samples) are still under investigation. This observation likely has important implications for understanding depositional and post-depositional history recorded in the rocks [4,5]. Though oxychlorine phases are likely not present in the VRR samples, different chlorine phases (e.g., akaganeite, trace chlorides) are indicated by EGA HCl evolutions (and APXS Cl measurements).

Overall, constraints on the nature and composition of VRR materials enabled by SAM EGA data, in the context of other mineralogical, geochemical, and strati-

graphic information obtained by the rover, inform hypotheses about the depositional and diagenetic history recorded in rocks of the VRR.

**References:** [1] Fraeman, A. A., et al. (2018) *LPSC*, abst. #1557. [1] Morris, R. V., et al. (2019), *this conference*. [2] Vaniman, D. T., et al. (2004), *Nature*, 431, 663. [3] Sutter et al. (2017), *J. Geophys. Res. Planets*, 122, 2574. [4] Archer, P. D., et al., (2019), *this conference*. [5] Sutter et al., (2019), *this conference*. [6] Sun, V. Z., et al. (2018) Fall AGU, P43A-10. [7] l'Haridon, J., et al. (2018) Fall AGU, P41A-07.