CONSTRAINTS ON THE MINERALOGY OF GALE CRATER MUDSTONES FROM MSL SAM EVOLVED WATER.

A. C. McAdam[1], B. Sutter[2,3], H. B. Franz[1,4], J. V. (Clark) Hogancamp [2,3,5], C. A. Knudson[1,6], S. Andrejkovicova[1,7], P. D. Archer[2,3], J. L. Eigenbrode[1], D. W. Ming[3], R. V. Morris[3], E. B. Rampe[3], T. F. Bristow[8], P. R. Mahaffy[1], R. Navarro-Gonzalez[9]. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, [2]Jacobs, Houston, TX 77058, [3]NASA/JSC, Houston, TX 77058, [4]CRESST, University of Maryland, Baltimore, MD 21228, [5]Geocontrols Systems Inc, Houston, TX, [6]CRESST, University of Maryland, College Park, MD, 20742, [7]CRESST, USRA, Columbia, MD, [8]NASA Ames Research Center, Moffiet Field, CA, 94035, [9]Universidad Nacional Autónoma de México, México, D.F. 04510.

Introduction: The Sample Analysis at Mars (SAM) and Chemistry and Mineralogy (CheMin) instruments on the Mars Science Laboratory (MSL) have analysed <150 µm fines from 14 sites at Gale Crater. Here we focus on the mudstone samples. Two were drilled from sites John Klein (JK) and Cumberland (CB) in the Sheepbed mudstone. Six were drilled from Murray Formation mudstone: Confidence Hills (CH), Mojave (MJ), Telegraph Peak (TP), Buckskin (BK), Oudam (OU), Marimba (MB). SAM's evolved gas analysis mass spectrometry (EGA-MS) detected H_2O, CO_2, O_2, H_2, SO_2, H_2S, HCl, NO, and other trace gases, including organic fragments. The identity and evolution temperature of evolved gases can support CheMin mineral detection and place constraints on trace volatile-bearing phases or phases difficult to characterize with X-ray diffraction (e.g., amorphous phases). Here we will focus on SAM H_2O data and comparisons to SAM-like analyses of key reference materials.

Methods: For SAM EGA-MS analyses, sample fines were heated to ~860°C at 35°C/min. 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_2O is represented by m/z 17, 18 or 20). The pressure in the oven was ~25 mb and the flow rate was ~0.8 sccm. For laboratory analyses, several systems were used to characterize a variety of phyllosilicates and other hydrated or hydroxylated materials under SAM-like conditions (SAM-like carrier gas, gas flow and gas pressure, temperature range and heating ramp rate). These included the SAM Testbed, a Pfeiffer HiQuad QMS coupled to a custom SAM-like pyrolysis oven, a Frontier PY-3030 pyrolyzer on an Agilent 5975C inert XL MS, or a Setaram LabSys Evo Thermogravimeter/Differential Scanning Calorimeter coupled to a Pfeiffer OmniStar QMS.

Results and Discussion: H_2O was the most abundant volatile released from all mudstone samples (~1-2 wt. % [e.g., 1, 2]). For JK and CB, most H_2O evolved <~450°C and has many potential sources, including adsorbed H_2O, smectite interlayer H_2O, structural H_2O/OH in salts and H_2O/OH in X-ray amorphous phases (poorly crystalline silicate or aluminosilicate phases (e.g., allophane, opal, glass), and/or nanophase Fe oxides/oxyhydroxides, Fig. 1b). H_2O evolved near 730°C is consistent with the dehydroxylation of a Fe saponite (Fig. 3b), in agreement with CheMin detection of a smectite [1]. (Note, JK and CB data not

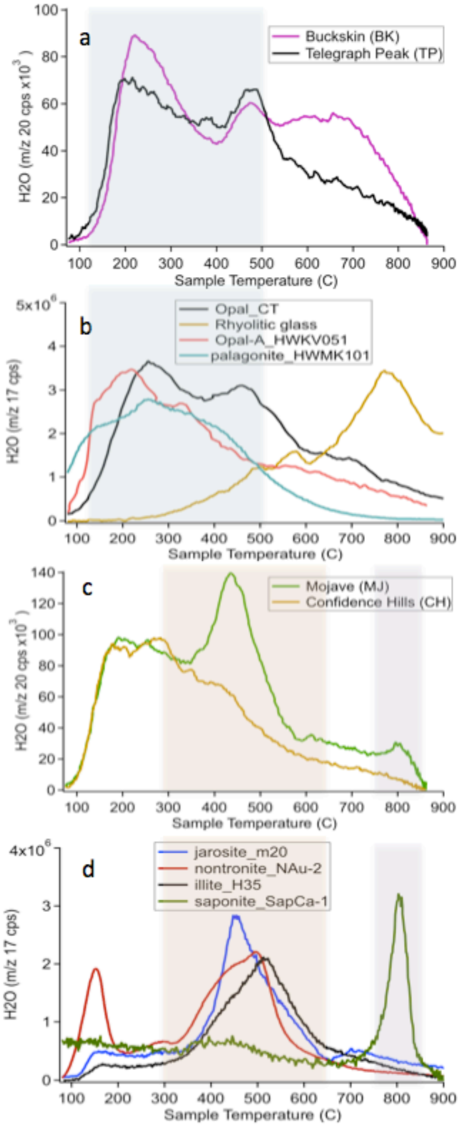

Fig 1. a) SAM EGA-MS data from BK and TP. b) SAM-like EGA-MS data from analog materials. c) SAM EGA-MS data from MJ and CH. d) SAM-like EGA-MS data from analog materials.

shown for brevity, see [1]). The position of the 02l XRD band of this Fe saponite (Griffith saponite) is similar to that in CheMin analyses of JK and CB [3].

For CH, MJ, TP, and BK as well, the majority of the H_2O was released <~500 ^{o}C (Fig. 1a and c), with similar potential sources as those listed above for JK and CB. In CH (Fig. 1c), the shoulder at ~450^{o}C could derive from the dehydroxylation of ~1 wt. % jarosite [4]. There could also be contributions to this shoulder, and to >450^{o}C H_2O, from the ~7.6 wt% phyllosilicate detected by CheMin [4]. Several phyllosilicates dehydroxylate near 450^{o}C (Fig. 1d), and at higher temperatures (Fig. 2b, 3b). The amount of H_2O evolved >450^{o}C is consistent with contributions from jarosite and the phyllosilicate (~14.6 ± 7.5 wt % smectite equivalent). In MJ, the small peak at ~800^{o}C is consistent with trioctahedral smectite dehydroxylation (e.g., saponite, Fig. 1c and 1d). The amount of H_2O evolved is approximately consistent with the ~4.7 wt. % smectite detected by CheMin [4] (~8 ± 3 wt% smectite equivalent). In MJ and TP, the large ~450^{o}C peak is consistent with jarosite dehydroxylation (~3.5 and ~1.5 wt. %, respectively [4]). In BK, amorphous phases contributing low temperature H_2O are likely dominated by silica-rich materials detected by CheMin [5] (e.g., opal-A, opal-CT and/or rhyolitic glasses); these materials may also contribute to >500^{o}C H_2O. H_2O evolved near 450^{o}C may result from jarosite present below CheMin detection limits.

In OU (Fig. 2a, 3a), most H_2O was released <500^{o}C and likely derives in part from the amorphous material and possible smectite interlayer H_2O, but unlike previous samples, gypsum (and likely bassanite) [6, 7] was also a contributor (Fig. 2b, blue area). The ~470^{o}C peak could result from phyllosilicate detected by CheMin [6] and would be consistent with nontronite (Fig. 2b, green area). In MB (Fig. 2a, 3a), most H_2O was released >500^{o}C and can be attributed to the phyllosilicates detected by CheMin [6, 8]. The peak at ~780^{o}C is most consistent with a trioctahedral smectite like saponite (Fig. 3b and [9]). The peak at ~610^{o}C is consistent with the dehydroxylation of a dioctahedral phase (e.g., some illites, Fig. 2b orange area and [9]). ChemCam analyses of Murray mudstones also suggest the possible presence of illite [10]. The small ~150^{o}C peak could have contributions from hydrated sulfates [6, 7], and smectite interlayer H_2O (see ~150^{o}C evolutions from smectites in Fig. 2b, 3b).

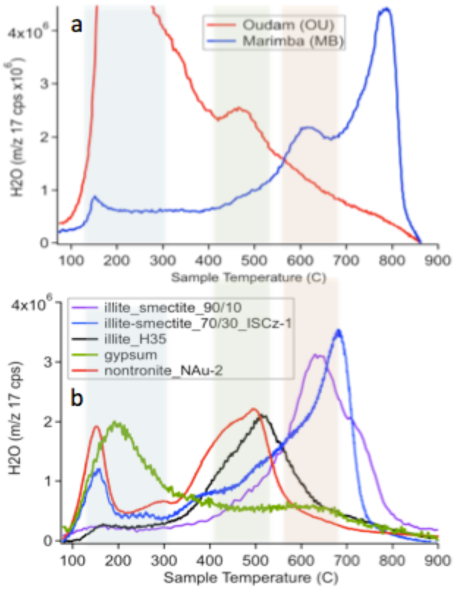

Fig. 2. a) SAM EGA-MS data from OU and MB. b) SAM-like EGA-MS data from analog materials.

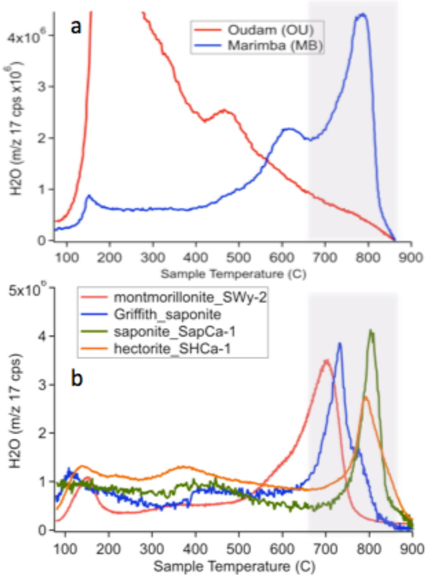

Fig. 3. a) SAM EGA-MS data from OU and MB. b) SAM-like EGA-MS data from analog materials.

Conclusions: SAM EGA-MS and SAM-like lab analyses of relevant analog materials can help to constrain the identity and abundance of hydrated or hydroxylated materials in Gale Crater samples. These insights into the mineralogy and geochemistry of the mudstones, in the context of the rich dataset provided by the array of MSL instruments, can enable constraints on the environmental history of Gale Crater.

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