

SAM-LIKE EVOLVED GAS ANALYSES OF PHYLLOSILICATE MINERALS AND APPLICATIONS TO SAM ANALYSES OF THE SHEEPBED MUDSTONE, GALE CRATER, MARS. A. C. McAdam¹, H. B. Franz¹, P. R. Mahaffy¹, J. L. Eigenbrode¹, J. C. Stern¹, A. E. Brunner^{1,2}, B. Sutter^{3,4}, P. D. Archer^{3,4}, D. W. Ming³, R. V. Morris³, D. L. Bish⁵, S. K. Atreya⁶ and the MSL Science Team. ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, ²Center for Research and Exploration in Space Science & Technology, University of Maryland, College Park, MD, 20742, ³NASA Johnson Space Center, Houston, TX, 77058, ⁴Jacobs, TX, 77258, ⁵Dept. of Geological Sci., Indiana Univ., Bloomington, IN 47405, ⁶University of Michigan, Ann Arbor, MI, 48109.

Introduction: While in Yellowknife Bay, the Mars Science Laboratory *Curiosity* rover collected two drilled samples, John Klein (hereafter “JK”) and Cumberland (“CB”), from the Sheepbed mudstone, as well as a scooped sample from the Rocknest aeolian bedform (“RN”). These samples were sieved by *Curiosity*’s sample processing system and then several subsamples of these materials were delivered to the Sample Analysis at Mars (SAM) instrument suite and the CheMin X-ray diffraction/X-ray fluorescence instrument. CheMin provided the first *in situ* X-ray diffraction-based evidence of clay minerals on Mars, which are likely trioctahedral smectites (e.g., Fe-saponite) and comprise ~20 wt% of the mudstone samples [1]. SAM’s evolved gas analysis (EGA) mass spectrometry analyses of JK and CB subsamples, as well as RN subsamples, detected H₂O, CO₂, O₂, H₂, SO₂, H₂S, HCl, NO, OCS, CS₂ and other trace gases evolved during pyrolysis. The identity of evolved gases and temperature(s) of evolution can augment mineral detection by CheMin and place constraints on trace volatile-bearing phases present below the CheMin detection limit or those phases difficult to characterize with XRD (e.g., X-ray amorphous phases). Here we will focus on the SAM H₂O data, in the context of CheMin analyses, and comparisons to laboratory SAM-like analyses of several phyllosilicate minerals including smectites.

Methods: For SAM EGA-MS analyses, delivered sample fines were nominally heated from ambient conditions in SAM (~30°C) to ~835°C at 35°C/min. For some SAM analyses, the sample heating approach involved holding at a given low temperature (termed a “boil-off”) followed by heating at a steady rate to ~835°C in order to mitigate the contributions of a component in the SAM instrument background to analyses (MTBSTFA [2,3]). Here we focus on H₂O traces from SAM runs in which no “boil-off” holds were used. Evolved gases were carried through manifold lines to the SAM QMS by a He carrier gas. The pressure of He in the oven was ~30 mb and the flow rate was ~0.8 standard cubic centimeters per minute. The SAM breadboard and other SAM-like EGA-MS laboratory systems, including the highest fidelity laboratory system – the SAM testbed, were used to characterize a variety of phyllosilicate reference materials

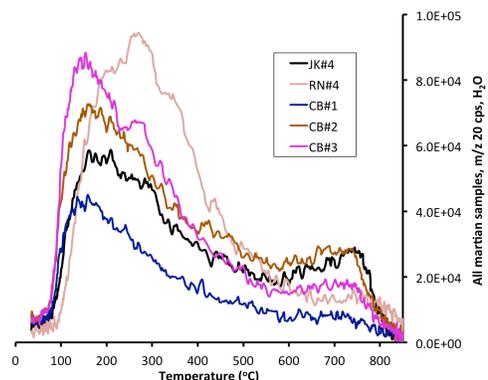


Fig 1. SAM EGA-MS H₂O traces from John Klein (JK), Cumberland (CB), and Rocknest (RN).

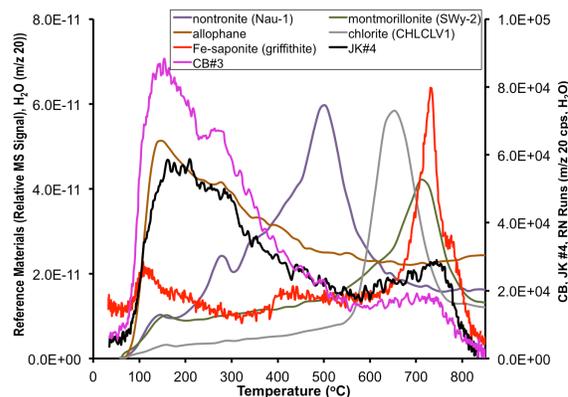


Fig. 2. SAM EGA-MS H₂O traces from JK and CB compared with selected H₂O EGA traces from several clay minerals acquired in SAM-like lab systems.

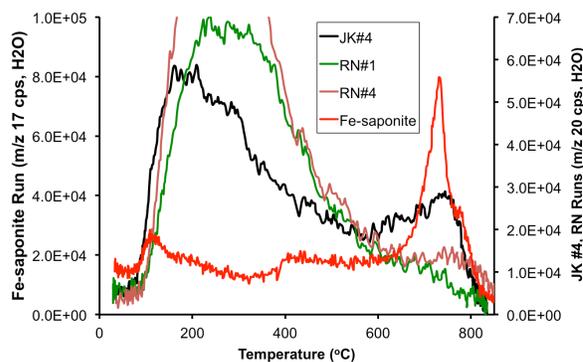


Fig. 3. SAM EGA-MS H₂O traces from RN and JK subsamples compared with H₂O EGA-MS trace from Fe-saponite (griffithite) acquired in the SAM testbed.

under SAM-like conditions (flight SAM-like carrier gas, gas flow and gas pressure conditions, temperature range and heating ramp rate). Several milligrams of <150 μm samples were analyzed.

Results and Discussion: H_2O was the most abundant volatile released from JK (1.8-2.4 wt%), CB (1.7-2.5 wt%) [4], and RN (1.6-2.4 wt%) [3], samples. The overall shape of the H_2O traces are similar for the three different samples, except for the more prominent high-temperature evolution near 750 $^\circ\text{C}$ for the JK and CB mudstone samples (Fig. 1). A majority of the H_2O comes off in a wide low-temperature peak <450 $^\circ\text{C}$. The low-temperature H_2O evolution has many potential sources, including adsorbed H_2O , smectite interlayer H_2O , and structural $\text{H}_2\text{O}/\text{OH}$ from bassanite and akaganeite (identified by CheMin [1]) and $\text{H}_2\text{O}/\text{OH}$ from X-ray amorphous phases in the sample (CheMin detected ~ 30 wt% amorphous phases in JK, CB, and RN samples [1,5]). The high-temperature H_2O near 750 $^\circ\text{C}$ is consistent with the evolution of H_2O from the dehydroxylation of the smectite clay mineral detected by CheMin.

Comparison with EGA-MS data collected under SAM-like conditions on a variety of clay mineral reference materials indicate that a trioctahedral smectite, such as Fe-saponite, is most consistent with the high-temperature H_2O evolution observed (Fig. 2). The Fe-saponite griffitite, a trioctahedral smectite with a low $\text{MgO}/(\text{FeO} + \text{Fe}_2\text{O}_3)$ ratio, was a high priority sample for SAM-like EGA-MS analyses because the position of its 021 X-ray diffraction band is similar to that reported for CheMin analyses of JK and CB samples (~ 22.5 deg 2θ Co $K\alpha$ radiation) [1].

The abundances of smectite clays indicated by SAM H_2O data also agree well with those determined from CheMin XRD patterns. If the abundances of H_2O released between 450 and 835 $^\circ\text{C}$ are assumed to result from smectite dehydroxylation, the wt% of smectites indicated in the samples analyzed by SAM (~ 16 -17 wt% \pm 11-12 wt%) [4] are consistent with the ~ 20 wt% obtained from CheMin data [1].

There may also be SAM EGA-MS evidence for a small high-temperature H_2O evolution from RN subsamples (Fig. 3). As in the mudstone samples, this evolution may indicate the presence of smectite clays. The idea of smectite clays in Rocknest materials is reasonable as some nearby rocks contain ~ 20 wt % smectites and the Rocknest aeolian deposit could be expected to have some input from local rocks. If present, such smectites must occur at abundances below the detection limit of CheMin for poorly ordered materials (<5 wt); larger abundances of smectite clays would have been identified from the CheMin analyses of Rocknest materials [5]. This potential detection

highlights the complementary nature of CheMin and SAM analyses for investigations of martian sample mineralogy.

Implications: The presence of the smectite clay minerals in the Sheepbed mudstone indicates relatively high water activity at the time of their formation (or during their transport and deposition if they are detrital clay minerals). These clay minerals are also consistent with waters having a near neutral pH and a low salinity. The fact that these clays are not chlorite indicates that their formation environment (and post formation environments) did not exceed $\sim 80^\circ\text{C}$ [e.g., 1]. These smectite clays are a key indicator of the presence of a past habitable environment at Yellowknife Bay which included alteration environments with favorable temperatures and fluid characteristics (pH, ionic strength, etc.) [e.g., 1, 6].

References: [1] Vaniman D.T. et al. (2013) *Science*, doi: 10.1126 /science.1243480. [2] Glavin D.P. et al. (2013) *JGR*, 118, 1955. [3] Leshin L.A. et al. (2013) *Science*, 341(6153), doi:10.1126/science.1238937. [4] Ming D.W. et al. (2013) *Science*, doi:10.1126/science.1245267. [5] Bish D.L. et al. (2013) *Science*, 341(6153), doi:10.1126 /science.1238932. [6] Grotzinger, J. P. et al. (2013) *Science*, doi: 10.1126/science.1242777.