
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 H$_2$O, CO$_2$, O$_2$, H$_2$, SO$_2$, H$_2$S, HCl, NO, OCS, CS$_2$ 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 H$_2$O 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 H$_2$O 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 H$_2$O traces from John Klein (JK), Cumberland (CB), and Rocknest (RN).](image1)

![Fig 2. SAM EGA-MS H$_2$O traces from JK and CB compared with selected H$_2$O EGA traces from several clay minerals acquired in SAM-like lab systems.](image2)

![Fig 3. SAM EGA-MS H$_2$O traces from RN and JK subsamples compared with H$_2$O EGA-MS trace from Fe-saponite (griffithite) acquired in the SAM testbed.](image3)
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:** H₂O 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 H₂O traces are similar for the three different samples, except for the more prominent high-temperature evolution near 750 °C for the JK and CB mudstone samples (Fig. 1). A majority of the H₂O comes off in a wide low-temperature peak <=450 °C. The low-temperature H₂O evolution has many potential sources, including adsorbed H₂O, smectite interlayer H₂O, and structural H₂O/OH from bassanite and akaganeite (identified by CheMin [1]) and H₂O/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 H₂O near 750 °C is consistent with the evolution of H₂O 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 H₂O evolution observed (Fig. 2). The Fe-saponite griffittite, a trioctahedral smectite with a low MgO/(FeO + Fe₂O₃) 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 20 Co Kα radiation) [1].

The abundances of smectite clays indicated by SAM H₂O data also agree well with those determined from CheMin XRD patterns. If the abundances of H₂O released between 450 and 835 °C are assumed to result from smectite dehydroxylation, the wt% of smectites indicated in the samples analyzed by SAM (~16-17 wt% ± 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 H₂O 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 ~80°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].