IDENTIFICATION OF PHYLLOSILICATES IN MUDSTONE SAMPLES USING WATER RELEASES DETECTED BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT IN GALE CRATER, MARS.

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Introduction: The Sample Analysis at Mars (SAM) instrument on board the Curiosity Rover has detected high temperature water releases from mudstones in the areas of Yellowknife Bay, Pahrump Hills, Naukluft Plateau, and Murray Buttes in Gale crater. Dehydroxylation of phyllosilicates may have caused the high temperature water releases observed in these samples. Because each type of phyllosilicate undergoes dehydroxylation at distinct temperatures, these water releases can be used to help constrain the type of phyllosilicate present in each sample.

CheMin XRD analyses have determined that the John Klein (JK), Cumberland (CB), Confidence Hills (CH), Mojave 2 (MJ2), Oudam (OU), and Marimba (MB) drilled samples contain detectable quantities of phyllosilicates [1]. JK, which was collected from the Sheepbed mudstone member of the Yellowknife Bay formation, contains 22 wt % smectite [1]. The JK XRD pattern has a broad 001 diffraction peak that extends from 12 to 9.4 Å which is characteristic of a 2:1 smectite. It has also been suggested that JK does not contain kaolinite, chlorite group minerals, or well crystallized phyllosilicates such as mica or illite [1]. CB, which was collected meters away from JK, contains 18 wt % smectite and has a similar diffraction pattern to JK. Both CB and JK possess 02*l* diffraction peaks most similar to saponite and possibly nontronite [1]. The 02*l* diffraction peaks from JK and CB are not similar to montmorillonite [1].

CH, which was collected from the Pahrump Hills, contains about 11 wt % phyllosilicate and is characterized by an XRD pattern with a 10 Å peak. Although the 10 Å peak is indicative of a collapsed smectite or poorly ordered 10 Å mineral, the 02*l* peak is obscured by pyroxene peaks and the exact variety is undeterminable using XRD [2]. Additionally, MJ2 contains about 4.7 wt % phyllosilicate.

OU was collected from near the Naukluft Plateau and contains 5 wt % phyllosilicates. MB, which was collected from the Murray Buttes area, contains 23 wt % phyllosilicates. Recent mudstone samples including OU and MB have produced XRD patterns distinct from Yellowknife Bay mudstones, and are indicative of the presence of dioctahedral phyllosilicate minerals in addition to trioctahedral phyllosilicate minerals [3]. In this study, Mars analogue phyllosilicate minerals were analyzed in the laboratory for their water releases and then compared to MB and OU in order to constrain the types of phyllosilicates present in these samples.

Materials and methods: Nine Mars analogue phyllosilicates were analyzed under SAM-like conditions. The minerals included montmorillonite (STx-1 from Clay Minerals Society (CMS)), nontronite (SWA-1 from CMS), beidelllite (from CMS), saponite (Sap-Ca-1 from CMS), griffithite (in basalt from Minerals Unlimited), and several varieties of illite (IMt-2, RM30, H35, and ISCz). The sample crucible and an identical empty crucible were placed in a Labsys EVO differential scanning calorimeter (DSC) furnace/thermal gravimeter (TG) connected to a Quadstar quadrupole mass spectrometer (QMS) configured to operate similarly to the SAM oven/QMS system. The DSC furnace was purged with helium gas and set to a pressure of approximately 30 mbar He. The crucibles were heated to 1000 ºC at a heating rate of 35 ºC/min and at a flow rate of 10 sccm He. Laboratory samples were analyzed for mass 18 releases and compared to mass 17, 18, 19, and 20 releases from MB and OU.

Results and Discussion: The SAM instrument analyzed the recently drilled OU (Sol 1361) and MB (Sol 1422) targets from phyllosilicate-bearing mudstones. These sediments produced high temperature water release peaks at 465 ºC (OU) and 611 ºC and 785 ºC (MB). The high temperature water releases are caused by the dehydroxylation of phyllosilicates. The temperature at which dehydroxylation occurred can help constrain which type of phyllosilicates the sample contained. Laboratory analyses of phyllosilicate minerals demonstrated that nontronite had a water release peak at 453 ºC, beidellite at 539 ºC, iron-rich illite (IMt-2) at 612 ºC, illite (RM30) at 633 ºC, illite (H35) at 527 ºC, illite-smectite (ISCz) at 698 ºC, montmorillonite at 702 ºC, griffithite at 813 ºC, and saponite at 837 ºC (Fig. 1).

OU produced a large water release with a peak at 189 ºC and a smaller water release peak at 465 ºC (Fig. 1). The release peak at 465 ºC, which is best observed with mass 17, is similar to nontronite, which produced a water release peak at 453 ºC. The release at 189 ºC may be caused by the presence of hydrous minerals such as gypsum (9 wt. % in OU) and/or the dehydration of phyllosilicate interlayer water.

MB produced a minor water release peak at 151 ºC, and two larger releases with peaks at 611 ºC and 785 ºC (Fig. 1). The low temperature water release may be caused by the presence of gypsum (9 wt. % in MB) or interlayer water. The high temperature releases from MB suggest that it could contain Fe-rich illite and saponite (var. griffithite) (Fig. 1). The presence of illite and griffithite, dioctahedral and trioctahedral phyllosilicates, respectively, also supports the XRD results from CheMin [3]. Additionally, the presence of illite is plausible based on data from APXS and ChemCam [4], however Fe-rich smectite may also produce water releases similar to the first high temperature water release in MB [5]. Further investigation is necessary to explore the possiblilty of Fe-rich smectite in MB.

Conclusion: Laboratory EGA analyses of phyllosilicate minerals demonstrated that water release data from SAM can be useful in constraining the phyllosilicate minerals present in a sample. Laboratory analyses suggested that OU contains nontronite and MB contains griffithite and Fe-rich illite. Having a more comprehensive view on the mineralogy and geochemistry of samples measured by SAM will help with future analogue laboratory experiments and in interpretations about the environment in Gale Crater (e.g., the diagenetic history of mudstones).

[1] Vaniman et al. (2014) *Science*, 341 DOI: 10.1126/science.1243480 [2] Cavanagh et al. (2015) LPSC XLVI #2735. [3] Bristow et al. (2017), LPSC XLVIII. [4] Mangold et al. (2017) LPSC XLVIII. [5] Brigatti (1982), *Clay Minerals*, 18.

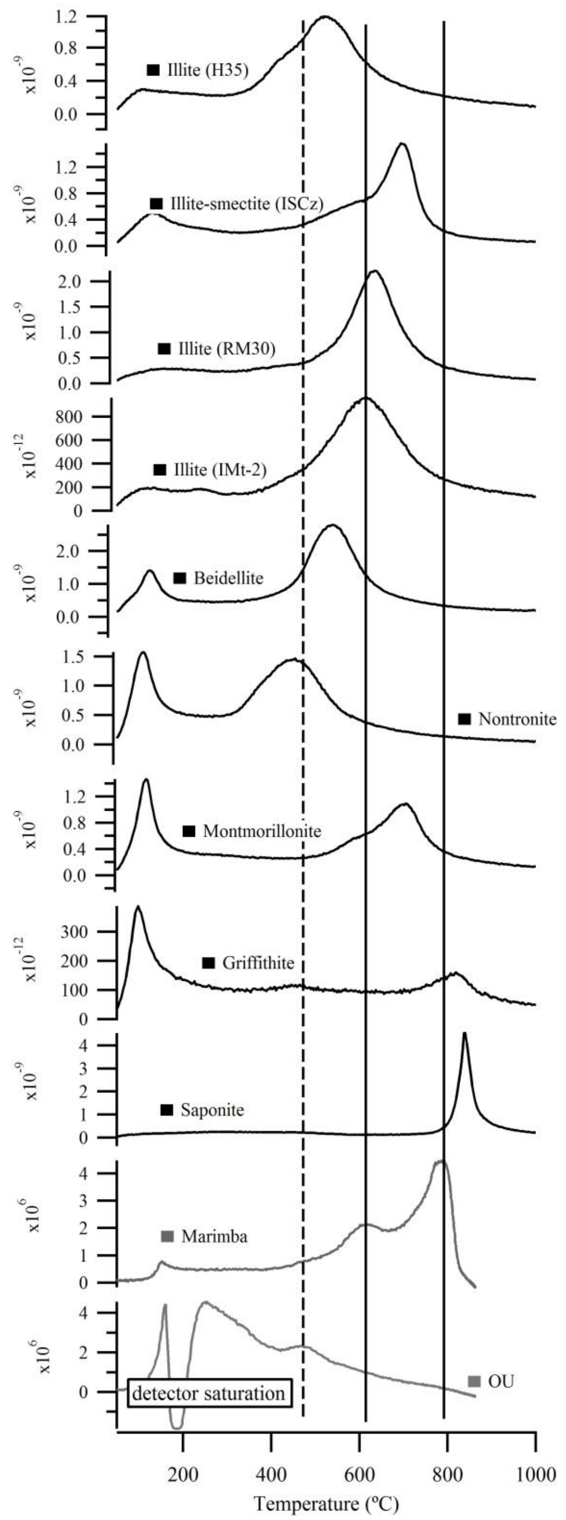

Fig. 1. Water releases from phyllosilicates compared to MB and OU. Y-axis shows water releases in mbar (experimental) or counts/sec (MB and OU). Solid and dashed vertical lines represent the locations of water release peaks detected in MB and OU, respectively. MB and OU plots use mass 17.