EVOLVED GAS ANALYSIS OF MARS ANALOG SAMPLES FROM THE ARCTIC MARS ANALOG SVALBARD EXPEDITION: IMPLICATIONS FOR ANALYSES BY THE MARS SCIENCE LABORATORY. A.C. McAdam¹, J.C. Stern¹, P.R. Mahaffy¹, D.F. Blake², T. Bristow², A. Steele³, H.E.F. Amundsen⁴, and the AMASE 2011 Team. ¹NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, ²NASA Ames Research Center, MS 239-4, Moffett Field, CA 94035, ³Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., Washington, DC 20015, ⁴Earth and Planetary Exploration Services, Jac Aalls gt 44b, N-0364 Oslo, Norway.

Introduction: The 2011 Arctic Mars Analog Svalbard Expedition (AMASE) investigated several geologic settings on Svalbard, using methodologies and techniques being developed or considered for future Mars missions, such as the Mars Science Laboratory (MSL). The Sample Analysis at Mars [SAM, e.g., 1] instrument suite on MSL consists of a quadrupole mass spectrometer (QMS), a gas chromatograph (GC), and a tunable laser spectrometer (TLS), which analyze gases created by pyrolysis of samples. During AMASE, a Hiden Evolved Gas Analysis-Mass Spectrometer (EGA-MS) system represented the EGA-QMS capability of SAM. Another MSL instrument, CheMin, will use x-ray diffraction (XRD) and x-ray fluorescence (XRF) to perform quantitative mineralogical characterization of samples [e.g., 2]. Field-portable versions of CheMin were used during AMASE.

AMASE 2011 sites spanned a range of environments relevant to understanding martian surface materials, processes and habitability. They included the basaltic Sverrefjell volcano, which hosts carbonate globules, cements and coatings [e.g.,3, 4], carbonate and sulfate units at Colletthøgda, Devonian sandstone redbeds in Bockfjorden, altered basaltic lava delta deposits at Mt. Scott Keltie, and altered dolerites and volcanics at Botniahalvøya. Here we focus on SAM-like EGA-MS of a subset of the samples, with mineralogy comparisons to CheMin team results. The results allow insight into sample organic content as well as some constraints on sample mineralogy.

Methods: The field EGA-MS system consisted of a Hiden HPR-20 QMS coupled to a custom-built sample oven. Powdered samples of ~10-100 mg were loaded into cleaned quartz boats and placed in the oven. Evolved gases were monitored as samples were heated at 20°C/min from ~50°C to ~1000°C, under SAM-like helium pressures (~30 mb) and gas flow conditions (~0.027 atmcc/sec). The identity of gases and temperature (T) of gas evolution can provide constraints on mineralogy and organic chemsistry. The instrument mass range is 1-300 Da, but here a "peak hopping" mode was utilized, in which several Da values of interest were monitored to achieve higher time sampling. The 20 Da and 45 Da (scaled) traces represent evolved H₂O and CO₂, respectively; 15, 27, 31, 39, 42 Da traces represent chain hydrocarbons (HCs) or their fragments; and 57, 71, 78 Da traces represent aromatic hydrocarbons (HCs) or their fragments.

Carbonates from Colletthøgda: The CO₂ EGA trace from the carbonate sample "KitKat" revealed a large peak from carbonate mineral breakdown at ~700°C (Fig. 1). This agrees with the finding of dolomite by the AMASE CheMin team. The EGA data also showed fragments of organic material evolving in roughly three different T ranges. Organic fragments evolved in the lowest T range, ~100-300°C, were likely loosely bound organics, absorbed or adsorbed to the rock matrix, and overall not as thermally mature as organics evolved in the mid-T range. Organics evolved in the mid-T range, ~300-600°C, were likely bound between grains in the rock matrix and/or more thermally mature than those evolved in the lower T range. Peaks in organic traces between ~600 and 800°C, coincident with CO₂ evolution from carbonate breakdown, probably represent organics which were trapped within the carbonate (e.g., in fluid inclusions). On Mars, encapsulation of any organics within minerals could play an important role in the preservation of organics, including possible biosignatures, against several types of environmental alteration (e.g., interactions with surface oxidants), and facilitate their detection by SAM EGA-MS, as well as SAM EGA-GCMS and/or EGA-TLS.

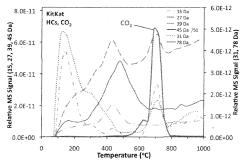


Fig. 1. Selected traces from Colletthøgda carbonate.

Altered Basaltic Materials from Scott Keltie: EGA analysis of the altered basaltic material AM11-155 revealed an H₂O trace with peaks at ~170°C and at ~400°C (Fig. 2). CheMin team analysis revealed a significant smectite clay-like component. EGA-MS allowed further constraints on the nature of this smectite-like phase. The general trend of a low T peak and a mid-range T peak is expected from EGA of a smectite clay mineral, but there are some differences. SAM-like EGA-MS analysis of a well-crystalline montmorillonite smectite clay, for example, shows a low T H₂O peak from adsorbed water, and a peak at ~650-700°C, resulting from dehydroxylation. Nontronite's dehydroxylation-related peak, however, will occur near 500°C. The mid-range T peak in AM11-155 at ~400°C may result from dehydroxylation of an overall more poorly-crystalline clay-like aluminosilicate phase. This is consistent with orange-hued palagonite (poorly-ordered alteration products of basaltic glass), in outcrop , and with the H₂O trace from SAM-like EGA of the palagonitic tephra JSC Mars-1 (not shown). The lower T peak in the Scott Keltie H₂O trace results from loosely-bound water. These results clearly illustrate how SAM-like EGA-MS and CheMin-like XRD can work together to inform sample mineralogy.

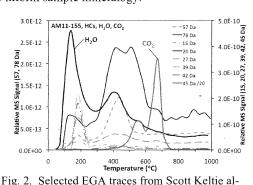


Fig. 2. Selected EGA traces from Scott Keltie altered basaltic materials.

Fragments of organic material evolved primarily in two different T ranges, with lesser amounts evolving in a third higher T range (~600-700°C) coincident with the CO₂ from carbonate breakdown (Fig. 2). Organic fragments evolved in the ~100-200°C range were likely loosely bound to the sample matrix and thermally immature. The low T peaks in organic fragment traces line up approximately with the large low T water trace peak from loosely bound water. Organic fragments evolved from ~300-600°C probably represent organics located between matrix grains and/or more thermally mature. Some of these organics may also be related to decomposition of the smectite-like phase near 400°C (H₂O release).

Phyllosilicate-bearing Sandstone from Bockfjord: The large, sharp peak near 560° C in the AM11-129 sandstone H₂O EGA trace (Fig. 3) is consistent with the dehydration of a non-smectite phyllosilicate mineral such as illite or chlorite, phases detected in several Redbed sandstone samples by CheMin team XRD. The peak in the CO₂ trace is consistent with calcite, which was also inferred in several Redbed samples by XRD. EGA data showed fragments of organic material, primarily in three different T ranges (Fig. 3). Unlike the samples discussed above, a significant evolution of organics between 100-300°C is not observed. Organic fragments evolved between 400-500°C were likely components of organics located between rock grains and relatively thermally mature. The apparent dominance of these relatively thermally mature organics is consistent with indications of low T metamorphism in some areas of the RedBeds (e.g., foliation). Smaller organic fragment trace peaks between ~500-600°C, and between ~700-850°C, are coincident with phyllosilicate dehydration and carbonate decomposition, respectively. These associations probably indicate organics were bound to their host phases and released during decomposition reactions.

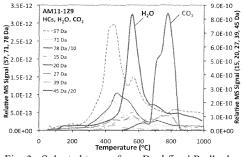


Fig. 3. Selected traces from Bockfjord Redbeds.

Conclusions: Associations between organics and geologic materials can influence their preservation potential and detection by in-situ investigations. Constraints on organic matter-mineral associations, and overall sample organic chemistry, enabled by our SAM-like EGA-MS analyses of these Mars analog samples demonstrate the potential to understand aspects of the organic chemical characteristics in materials sampled by MSL, even when utilizing the simplest type of solid sample experiment SAM will perform. Any organic chemical information inferred from EGA analysis could then also be followed by detailed EGA-GCMS and/or EGA-TLS experiments.

As illustrated by the above Mars analog studies, SAM EGA-MS can also be expected to support and, in some cases, supplement CheMin-derived mineralogical analyses of martian surface materials sampled by MSL. Key potential contributions may include additional constraints on minor abundances of volatile-bearing minerals or additional insights into the crystallinity of clays or clay mineraloid phases detected. Overall, the types of secondary minerals in a martian assemblage, as well as the nature (e.g., crystallinity) of those phases, can help constrain alteration conditions. By making detailed comparisons between SAM-like and CheMin-like analyses of Mars analogs and better understanding any mineralogical constraints obtained, we aim to provide information that will be directly relevant to interpretation of MSL flight data.

References: [1] Mahaffy P.R. (2008) Space Sci Rev., 135, 255. [2] Blake D.F. (2010) Geochem. News [3] Steele A. et al. (2005) LPS XXXVI, Abstract #2173. [4] Treiman A. H. et al. (2002) EPSL, 204, 323.

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