

FIELD CHARACTERIZATION OF THE MINERALOGY AND ORGANIC CHEMISTRY OF CARBONATES FROM THE 2010 ARCTIC MARS ANALOG SVALBARD EXPEDITION BY EVOLVED GAS ANALYSIS.

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Introduction: The 2010 Arctic Mars Analog Svalbard Expedition (AMASE) investigated two geologic settings using methodologies and techniques being developed or considered for future Mars missions, such as the Mars Science Laboratory (MSL), ExoMars, and Mars Sample Return. The Sample Analysis at Mars (SAM) [1] instrument suite, which will be on MSL, consists of a quadrupole mass spectrometer (QMS), a gas chromatograph (GC), and a tunable laser mass spectrometer (TLS); all will be applied to analyze gases created by pyrolysis of samples. During AMASE, a Hiden Evolved Gas Analysis-Mass Spectrometer (EGA-MS) system represented the EGA-MS 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 2010 focused on two sites that represented “biotic” and “abiotic” analogs. The “abiotic” site was the basaltic Sigurd fjell vent complex, which contains Mars-analog carbonate cements including carbonate globules which are excellent analogs for the globules in the ALH84001 martian meteorite [e.g., 3, 4]. The “biotic” site was the Knorring fjell fossil methane seep, which featured carbonates precipitated in a methane-supported chemosynthetic community [5]. This contribution focuses on EGA-MS analyses of samples from each site, with mineralogy comparisons



Figure 1 (left). Knorring fjell sample, a) black lithology and b) green lithology. Figure 2 (right). Sigurd fjell sample, c) carbonate crust surface layer and d) basalt.

to CheMin team results. The results give insight into organic content and organic-mineral associations, as well as some constraints on the minerals present.

Methods: The field EGA-MS system consisted of a Hiden Analytical HPR-20 QMS coupled to a custom-built sample oven. Powdered rock samples of ~7-15

mg were loaded into cleaned quartz boats and placed into the oven. SAM-like helium pressures (~30 mb) and gas flow conditions (~0.027 atm-cc/min) were used. Evolved gases were monitored as samples were heated at 20°C/min from ~50°C to ~950°C. The identity of evolved gases and the temperature of gas evolution can provide constraints on sample mineralogy and organic chemical characteristics. 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.

Organic materials and organic-mineral associations: Organic materials evolved from all samples over a range of temperatures (Ts). In general, this can indicate that the organics have a range of thermal maturity and/or are bound in different ways to their rock matrix (the organics can be outside of grains or minerals (here termed *intermineral*) or encapsulated within minerals (*intramineral*)). Most often, *intermineral* organics are the dominant pool of organic material inferable from the EGA-MS analyses, and *intramineral* organics can be more difficult to infer with EGA-MS alone.

For example, analyses of both Knorring fjell lithologies (Fig. 1) revealed organic material evolving from the sample (e.g., alkane fragments, benzene) over a range of Ts (Figs. 3 and 4). Much of it is probably *intermineral*, and is evolved at different Ts because of different degrees of thermal maturity of the material. In the green lithology, some benzene is evolved near the same T as the CO₂ peak (Fig. 3). Benzene could have evolved in this T range because the organics giving rise to the benzene release were trapped inside the carbonate mineral and released when it broke down. However, it is also possible that these molecules happened to be fragments of more complex structures that did not breakdown until that T. The majority of the benzene comes off at a lower temperature, around 500-600°C, which is common in natural samples.

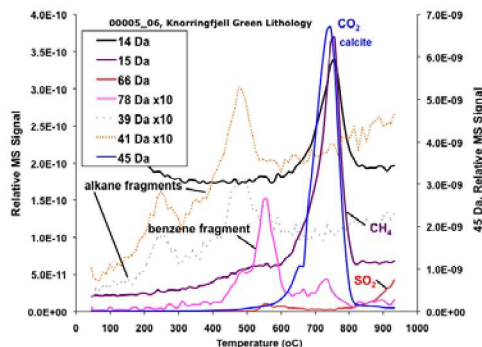


Figure 3. EGA traces from Knorring fjell green lithology.

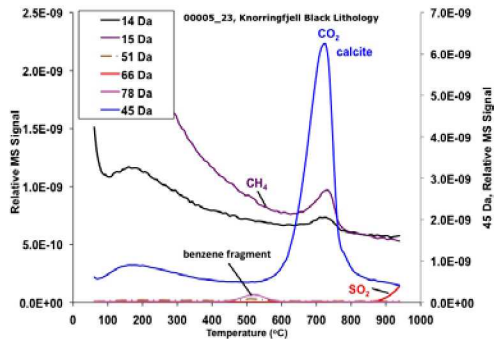


Figure 4. EGA traces from Knorringfjell black lithology.

Mass 15, which can be attributed to methane, is possibly an exception to this. Methane loosely trapped in a sample, being the smallest alkane as well as a gas under ambient conditions, would be expected to be released at low Ts on heating the sample. The 15 Da EGA curves for both Knorringfjell lithologies indicate some low T methane release, but there is a peak in release corresponding to the CO₂ peak (Figs. 3 and 4). This may indicate that some methane was *intramineral* (e.g., in a fluid inclusion) and released on carbonate mineral breakdown. Fluid inclusions were observed with optical microscopy in sections of Knorringfjell rocks.

EGA of a sample from the outer layer of a carbonate crust on a basalt from Sigurdfjell (Fig. 2, labeled c) also reveal organic material evolving over a range of Ts (Fig. 5). A significant mass 29 (likely dominated by CO) peak occurred between 300 and 350°C (Fig. 5). This peak coincides with a mass 20 (water) peak around 300°C that results from goethite (2% goethite was detected by CheMin XRD). The goethite may have enabled the increased oxidation of organics to CO during the run. The EGA data from the Sigurdfjell basalt underneath the carbonate crust (Figure 2, labeled d) also showed organics over a range of temperatures, dominated by benzene around 500°C (Fig. 6).

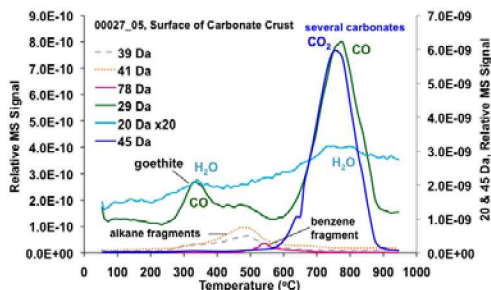


Figure 5. EGA traces from Sigurdfjell carbonate crust.

Minor mineralogy: The 66 Da traces from Knorringfjell samples (Fig. 3 and 4) indicated SO₂ coming off near 950°C. This SO₂ peak likely derives from a minor sulfide or sulfate mineral in the sample, though

CheMin did not observe any sulfates or sulfides. This may be because it was not present in their subsamples or it may be present but below the detection limit.

In the Sigurdfjell basalt sample, a peak around 600-650°C in the mass 45 (CO₂) trace indicated a minor Fe- and/or Mg- carbonate mineral not detected by CheMin (Fig. 6). This small amount of carbonate could be attributed to the carbonate globules known to be often present in these basalts [e.g., 3, 4]. The higher T CO₂ peak occurs at a higher T than expected for the breakdown of any common carbonate mineral during our SAM-like EGA conditions. This CO₂ could be from cracking of the igneous minerals or glass present in the basalt which contained trapped magmatic CO₂

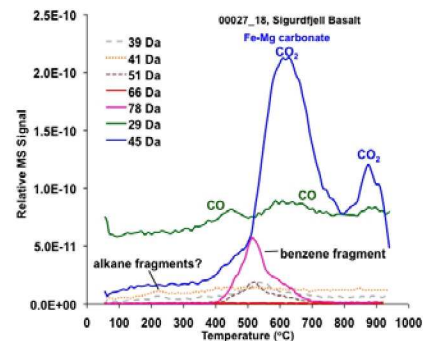


Figure 6. EGA traces from Sigurdfjell basalt.

(in fluid inclusions or inside crystal structures).

Implications: How organics are associated with geologic materials can affect their susceptibility to alteration and preservation potential, as well as their detection by *in-situ* exobiology investigations. As such, these associations are expected to have a large impact on the preservation and detection of any biosignatures or prebiotic chemistry on other worlds. Constraints on organic matter-mineral associations, and overall sample organic chemistry, enabled by our MSL-like analyses of these Mars-analog samples highlight the potential to explore these organic chemical characteristics in samples on the surface of Mars with landed missions.

Minor minerals in an assemblage can be useful in constraining rock or soil formation scenarios. CheMin is the primary mineralogical tool on MSL, and the field-portable version is one of the main mineralogical tools on AMASE, as well. EGA, both with MSL/SAM on Mars and during AMASE, can aid in constraining minor mineralogy in samples where minor minerals which release a detectable gas during pyrolysis are present near or below the CheMin detection limit

References: [1] Mahaffy P. R. (2008) *Space Sci Rev.*, 135, 255. [2] Blake D. F. et al. (2009) *LPS XL*, Abstract #1484. [3] Treiman A. H. et al. (2002) *EPSL*, 204, 323. [4] Steele A. et al. (2005) *LPS XXXVI*, Abstract #2173.

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