DOLOMITE SAMPLE FROM SVALBARD, NORWAY, ANALYZED USING THE PYROLYSIS PROTOCOL OF THE SAM INSTRUMENT. O. Botta[1,2], K. E. Fristad[2], P. R. Mahaffy[2], J. Eigenbrode[2,3], Andrew Steele[3] and the AMASE 2006 Team. [1]International Space Science Institute, Hallerstrasse 6, CH-3012 Bern, Switzerland (botta@issibern.ch), [2]NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, USA, [3]Geophyscial Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd, NW, Washington, DC 20015, USA.

Introduction: The goals of Arctic Mars Analogue Svalbard Expeditions (AMASE) are to test portable instruments for their robustness as field instruments for in situ life detection, to assess the Mars analogue environments for signs of life, to refine protocols for contamination reduction and to understand the effects of transport on sample integrity by assessing bioloads immediately in the field. These results are then compared with laboratory measurements made after transportation. For the most recent expedition, AMASE 2006, additional high-level goals included to examine-examination of measurement techniques and protocols that are candidates for future Mars missions or are presently under development for the 2009 Mars Science Laboratory (MSL) under a NASA grant from the Astrobiology Science and Technology for Exploring Planets (ASTEP) budget line. NASA Goddard Space Flight Center (GSFC) is developing the Sample Analysis at Mars (SAM) instrument for incorporation into MSL. Specifically, the the SAM instrument's primary goals for SAM on AMASE-2006 were

1) to develop measurement techniques and protocols to be used on the SAM instrument,

2) to refine analytical procedures for Mars analog material testing,

3) to coordinate analytical efforts and data interpretation with other instruments to simulate an operational scenario for the MSL mission, and

4) to deploy a SAM prototype in the field.

Instruments: During the AMASE 06 expedition, a semi-portable *Griffin* gas chromatograph/ion trap-mass spectrometer (GC-ITMS) equipped with a MXT-5 column (Varian, 30 m, 0.25 mm ID, 0.12 mm film thickness) was used for sample analysis, and Helium was used as the carrier gas. A commercial pyrolysis system was interfaced to the GCMS that utilized a quartz sample cup that could be heated from ambient to 1100 °C, the operation conditions to be used for pyrolysis on Mars with SAM. The instrument was used primarily on the research vessel, but at one occasion was deployed in the field as well. After the expedition, samples were analyzed at GSFC using both the *Griffin* as well as the *Finnigan* GC-quadrupole-MS (QMS) with the same type of column.

Experimental: Samples from the different locations were acquired using sterilized tools (chisel, scoop, spatula). In addition, one sample was acquired by the CliffBot rover during its first deployment. The samples were collected in baked aluminium (500°C, 4h) foil. Direct contact with the samples was avoided at all times. In order to maximize the surface area, samples that were not in powder form were crushed using sterile, agate mortar and pestle.

For pyrolysis analysis, a commercial pyroprobe system comprised of a pyrolysis unit (PU) and a pyroprobe with an associated electronics box was installed on the GC-MS systems. A sterilized quartz boat loaded with approx. 50 mg sample aliquot was carefully installed inside the pyroprobe. The loaded pyroprobe was inserted into the pyrolysis unit (PU), which was then purged with helium (He) and heated to 200 °C. After the GC-MS system was initiated and ready, the pyroprobe was commanded to heat the coil and boat to 1100 °C at maximum power and to hold it there for 10 minutes while the GC-MS time program was started simultaneously. Chromatographic peaks were identified in Selective Ion Mass chromatograms using literature data [1] and the Xcalibur software package in connection with the NIST mass spectra library Mass Search 2.0.

The same procedures were applied for analyses performed after the expedition with collected samples at GSFC. In addition to the pyrolysis procedures applied during the expedition, step-wise thermal desorption experiments were carried out where the pyroprobe and boat with the samples were subsequently heated to temperatures of 300 °C, 450 °C, 700 °C, 900 °C and 1100 °C and the volatiles were analyzed with the GC-QMS at each temperature step.

Results and Discussion: A total of 55 GC-MS analyses, both pyrolysis and extraction/derivatization, were performed during the AMASE 2006 expedition on board R/V *Lance*. Here we focus on the detection and characterization of organic compounds in samples from the Ebbadalen Formation, specifically of a dolomite sample collected in that area.

Chromatograms in the Total Ion Current (TIC) mode as well as the Reconstructed Ion Current (RIC) modes are shown in Fig. 1 and 2. Fig. 1 are the chro-

matograms from the *Griffin* GC-ITMS, while Fig. 2 shows data from the *Finnigan* GC-QMS after step-heating. Note that the retention time scales are different, and that the intensities between the two instruments can not be compared.

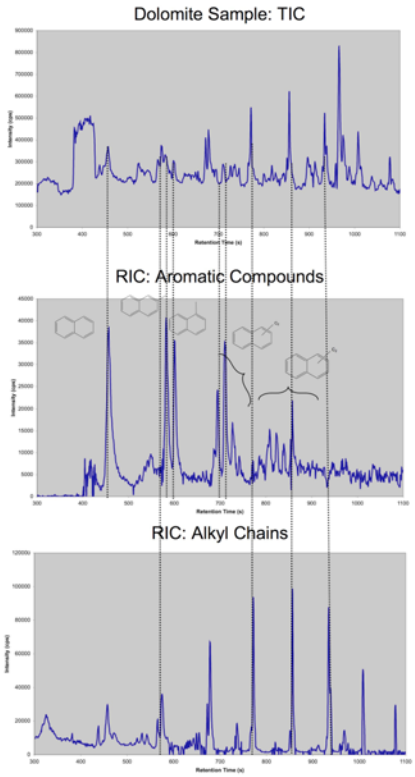

Figure 1. Total Ion Current (TIC) and Reconstructed Ion Current (RIC) Chromatograms of the a Dolomite Sample from Ebbadalen, Svalbard, analyzed on the *Griffin* GC-ITMS using the one-step heating pyrolysis protocol of the SAM instrument to 900 °C.

Simple aromatic compounds such as naphthalene and methylated naphthalene were detected using the SAM pyrolysis protocol using the *Griffin* GC-ITMS. Also, an envelope of aliphatic chains using a RIC at m/z=57 was identified (Fig. 1). Using the Finnigan GC-QMS, higher hydrocarbons such as phenanthrene, fluorene and dibenzothiophene in addition to an extended envelope of aliphatic hydrocarbons were detected (Fig. 2). The molecular composition matches expectations for a hydrocarbon–rich dolomite [3] like those in the Carboniferous Ebbadalen Fm. Although these specific compounds (Fig. 1 and 2) are decomposition products of biological material on Earth, they are ambiguous biosignatures under other conditions. Biomarkers diagnostic of life are still under investigation using both methods.

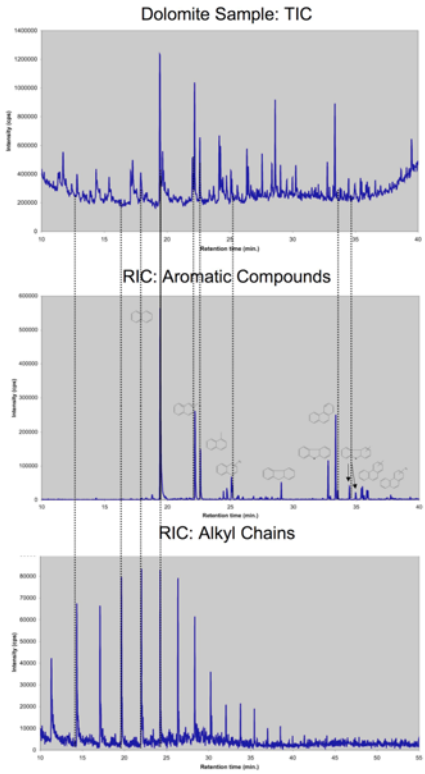

Figure 2. Total Ion Current (TIC) and Reconstructed Ion Current (RIC) Chromatograms of the a Dolomite Sample from Ebbadalen, Svalbard, analyzed on the *Finnigan* GC-QMS using the step-wise heating pyrolysis protocol of the SAM instrument (steps at 300, 450 and 700 °C before heating to 900 °C).

Conclusions. The sampling and pyrolysis protocols for the SAM instrument were successfully tested during the AMASE 2006 expedition. Naphthalene, phenanthrene as well as their methyl, dimethyl and trimethyl isomers were detected in a hydrocarbon-rich dolomite sample from the Ebbadalen Fm. These experiments are essential in the development of SAM pyrolysis protocols for the analysis of organic compounds on Mars.

References: [1] Eigenbrode J. (2004), Ph.D. thesis, Appendix G, Pennsylvania State University. [2] Jiang, C. (1998), Ph.D. thesis, Curtin University of Technology. Hunt, J. (1995) Petroleum Geochemistry and Geology, W.H. Freeman Co., pp.743.

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