EVOLVED GAS ANALYSIS AND X-RAY DIFFRACTION OF CARBONATE SAMPLES FROM THE 2009 ARCTIC MARS ANALOG SVALBARD EXPEDITION: IMPLICATIONS FOR MINERALOGICAL INFERENCES FROM THE MARS SCIENCE LABORATORY.

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Introduction: The 2009 Arctic Mars Analog Svalbard Expedition (AMASE) investigated several 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 (MSR). AMASE-related research comprises both analyses conducted during the expedition and further analyses of collected samples using laboratory facilities at a variety of institutions. The Sample Analysis at Mars (SAM) instrument suite, which will be part of the Analytical Laboratory on MSL, consists of a quadrupole mass spectrometer (QMS), a gas chromatograph (GC), and a tunable laser spectrometer (TLS). An Evolved Gas Analysis Mass Spectrometer (EGA-MS) was used during AMASE to represent part of the capabilities of SAM. The other instrument included in the MSL Analytical Laboratory is CheMin, which uses X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) to perform quantitative mineralogical characterization of samples [e.g., 1]. Field-portable versions of CheMin were used during the AMASE 2009.

A major focus of AMASE has been on understanding the formation of carbonates from several volcanoes on Spitsbergen, Norway (e.g., the Sverrefjell volcano) Carbonate globules from these analog sites bear striking similarities to those in the martian meteorite ALH84001, including similarities in morphology, mineral associations, carbonate mineralogy, mineral zoning, and the presence in some globules of macromolecular carbon associated with magnetite [2,3,4].

Here, we discuss the preliminary interpretation of EGA and XRD analyses of selected AMASE carbonate samples and implications for mineralogical interpretations from MSL. Though CheMin will be the primary mineralogical tool on MSL, SAM EGA could be used to support XRD identifications or indicate the presence of volatile-bearing minerals which may be near or below XRD detection limits. Data collected with instruments in the field and in comparable laboratory setups (e.g., the SAM breadboard [5]) will be discussed.

Methods: Field EGA-MS studies were conducted using a Hiden Analytical HPR-20 QMS coupled to a GSFC-built pyrocell. Powdered samples were taken from layered carbonate rocks by dremeling and then sieved to <150 um. Samples of 10 to several 10s of mg were then used in the EGA setup and in the field versions of CheMin [1]. SAM-like helium pressures (~30 mb) and gas flow conditions (~0.027 atm-cc/min) were maintained in the pyrocell during EGA runs. Evolved gases were monitored as samples were heated at a constant temperature ramp of 40°C/min from ~20°C to ~1000°C. The combination of which gases are evolved from a sample and the temperature at which a gas evolves can give constraints on the mineralogy of a sample. The mass range of the instrument is 1-300 dalton, though a 1-150 dalton range was typically targeted for better time sampling. Though not the focus of this abstract, this range also allowed analysis of low mass organics evolved from samples on heating. The results and implications of the organic material analyses will be discussed in future contributions.

Preliminary Results and Discussion: EGA traces of evolved CO_2 (mass 44) from layers 1, 2, 4, and 7-9 of the AMASE sample SV04-00020 are displayed in Fig. 1. Differences in peak top temperatures, peak onset temperatures, and peak shapes due to overlapping peaks indicate differences in carbonate mineralogy between different layers. Overall, this is consistent with mineralogy results from XRD, which indicated: Layer 1- 75% dolomite, 25% ankerite; Layer 2- 100% ankerite; Layer 4- 100% ankerite; Layer 7-9- 49% dolomite, 29% magnesite, 17% montmorillonite, 3% calcite, 2% siderite.

Work to more precisely tie EGA peak top/onset temperatures and peak areas to carbonate minerals and mineral abundances in natural mineral mixtures is ongoing. An important consideration is how to ensure that homogeneous representative samples of thin rock layers are delegated to each instrument. Some observed mineral differences could be due to heterogeneity of the mineralogy within a sampled layer, and not to differences in the measurement abilities of an instrument or to differences in interpretation of data from different instruments. This is a relevant consideration for analyses of martian samples that will be done by SAM and CheMin on MSL, as well, though this issue may be mitigated by looking at more bulk samples.

An EGA trace of H_2O (mass 18) from layer 7-9 in SV04-00020 is presented in Figure 2. The number of

peaks and peak top and onset temperatures are consistent with water evolution from a smectite clay mineral. The lower temperature peaks are generally consistent with dehydration of adsorbed and interlayer water from a smectite clay. The broad higher temperature peak, though small, is more consistent with a montmorillonite-like smectite than a nontronite-like smectite, because the peak temperature is more consistent with dehydroxylation of Al-OH in smectite octahedral sites than with dehydroxylation of Mg-OH or Fe-OH in octahedral sites. The EGA trace supports the XRD identification of montmorillonite in this layer.

EGA traces of CO_2 (mass 45) from layers 1 and 2 of a different AMASE carbonate sample from "Fleece Cave" (SVBK09004) are displayed in Figure 3. While peak shapes appear similar, the differences in peak widths and peak top and onset temperatures indicate differences between the mineralogy of Layer 1 and 2. This is consistent with XRD data which indicated the two layers have mineralogical differences, specifically: Layer 1-42% ankerite, 30% siderite, 25% calcite, 3% aragonite; Layer 2-66% dolomite, 30% magnesite, 4% rhodocrosite.

The EGA trace of SO_2 (mass 64) from layer 2 of this SVBK09004 sample (Figure 4) indicates the presence of a sulfide or sulfate mineral, though no sulfur-bearing phases were observed with XRD. This is likely because the phase is a trace component, an assertion supported by the small amounts of SO_2 evolved.

Implications: These examples of analyses of complex Mars-analog carbonate samples by field and laboratory instruments aimed at mimicking aspects of the SAM and CheMin instruments on MSL highlight the potential of SAM EGA and CheMin XRD analyses to be highly complimentary. EGA can be used to support identification of volatile-bearing phases by XRD. It may be especially useful to support the identification of low abundances of clay minerals in a complex mixture by XRD. EGA can also be utilized to study trace phases in martian samples which are below the XRD detection limit, if such phases are present.

References: [1] Blake D. F. et al. (2009) *LPS XL,* Abst. #1484. [2] Amundsen H. E. F. (1987) *Nature, 327,* 692. [3] Steele A. et al. (2007) *MAPS, 42,* 1549. [4] Treiman A. H. et al. (2002) *EPSL, 204,* 323. [5] Mahaffy P. R. and Franz H. B. (2006) *Martian Sulfates Rec. Atm-Fld-Rock Int.,* Abst. #7014.
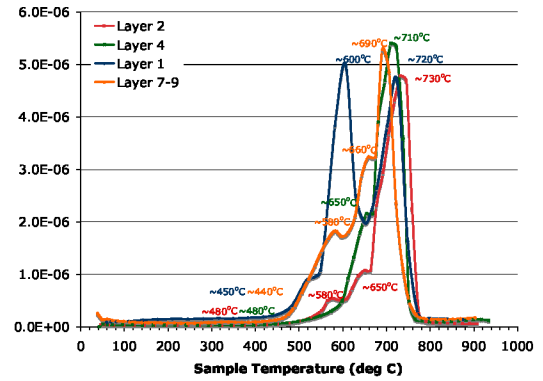
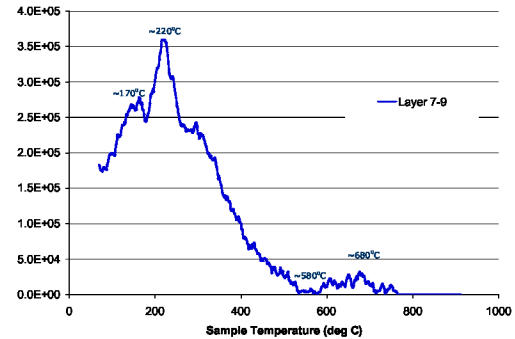Figure 1. EGA traces of CO_2 from layers of SV04-00020.

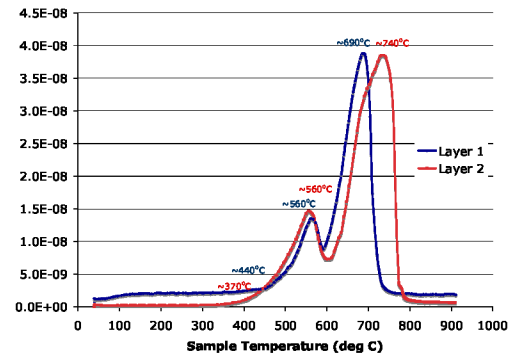Figure 2. EGA trace of H_2O from Layer 7-9 in SV04-00020, consistent with a montmorillonite-like smectite clay.

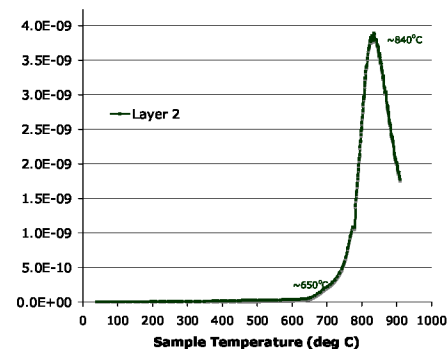Figure 3. EGA traces of CO_2 from layers of SVBK09004.

Figure 4. EGA trace of SO_2 from Layer 2 of SVBK09004, indicating a sulfide or sulfate mineral.