

$\delta^{13}\text{C}$ ANALYSIS OF MARS ANALOG CARBONATES USING EVOLVED GAS – CAVITY RINGDOWN SPECTROMETRY ON THE 2010 ARCTIC MARS ANALOG SVALBARD EXPEDITION (AMASE).

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Introduction: The 2010 Arctic Mars Analog Svalbard Expedition (AMASE) investigated two distinct geologic settings on Svalbard, using instrumentation and techniques in development for future Mars missions, such as the Mars Science Laboratory (MSL), ExoMars, and Mars Sample Return (MSR). The Sample Analysis at Mars (SAM, e.g. [2]) instrument suite, which will fly on MSL, was developed at Goddard Space Flight Center (GSFC), together with several partners. SAM consists of a quadrupole mass spectrometer (QMS), a gas chromatograph (GC), and a tunable laser spectrometer (TLS), which all analyze gases created by evolved gas analysis (EGA).

The two sites studied represent “biotic” and “abiotic” analogs; the “biotic” site being the Knorringfjell fossil methane seep, and the “abiotic” site being the basaltic Sigurdfjell vent complex. The data presented here represent experiments to measure the carbon isotopic composition of carbonates from these two analogs using evolved gas analysis coupled with a commercial cavity ringdown CO_2 isotopic analyzer (Picarro) as a proxy for the TLS on SAM.

Methods: On AMASE 2010, we simulated SAM’s capability to measure the isotopic composition of CO_2 from the thermal decomposition of planetary regolith by using a Hiden EGA-MS system and a Picarro Cavity Ringdown CO_2 isotope analyzer.

The Hiden EGA-MS system utilizes a Hiden Ana-

lytical HPR-20 quadrupole mass spectrometer coupled to a GSFC-built manifold and pyrocell capable of heating samples to a maximum of 1100°C . Gases are monitored by the mass spectrometer as they are evolved on heating relevant samples at a constant temperature ramp from approximately room temperature to an upper temperature ranging from 950 to 1100°C .

Cavity Ringdown Spectrometry (CRDS) has recently been made commercially available in benchtop form. Our system is designed to model TLS measurements of CO_2 evolved from pyrolysis on SAM. A Picarro CO_2 analyzer CRDS was used to measure the carbon isotopic composition of CO_2 evolved from the heating of samples using the GSFC-built pyrocell on the Hiden EGA-MS system. The EGA-MS setup has a manifold to capture CO_2 in an evacuated stainless steel cylinder upon detection via the Hiden Analytical HPR-20 quadrupole mass spectrometer.

The commercial CRDS analyzers (Picarro and Los Gatos Research) are designed to measure the concentration and isotopic composition of atmospheric CO_2 . CRDS measures the decay of the intensity of a laser beam in the presence of CO_2 gas as it is bounced back and forth between two highly polished mirrors. CRDS is usually operated as a flow through instrument where the sample is pumped through the cavity, but may also be valved off and operated in “batch” mode, by evacuated the cavity and filling it with gas to the appropriate

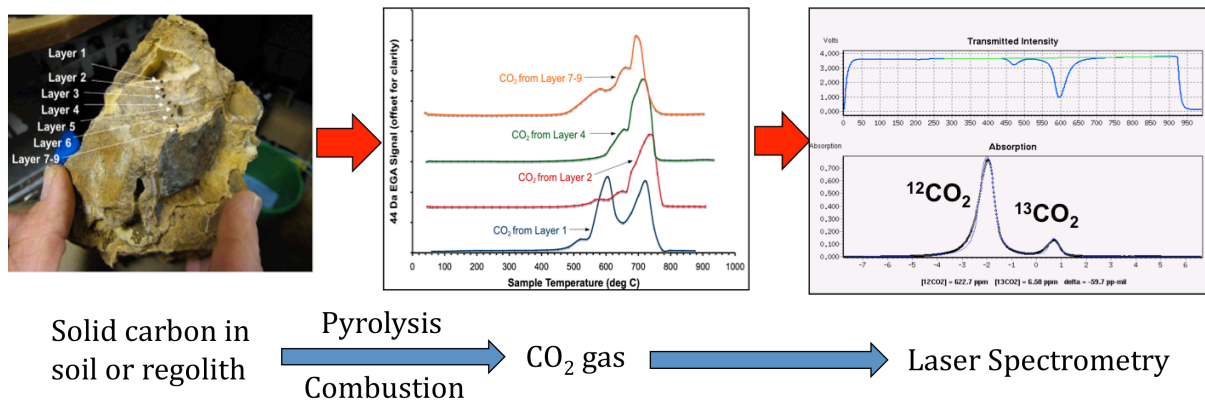


Figure 1: Procedure for measurement of CO_2 evolved from the thermal decomposition of carbonates. Samples are powdered, heated in the GSFC-built pyrolysis oven to $\sim 1000^\circ\text{C}$ while being monitored by the mass spectrometer. The CO_2 is captured in an evacuated stainless steel cylinder and introduced into a Picarro or LGR CO_2 isotope analyzer to obtain $\delta^{13}\text{C}$.

pressure and interrogating the gas in static mode.

EGA-CRDS experimental protocol

Samples were first characterized by EGA and mass spectrometry to determine the amount of CO₂ evolved during thermal decomposition. Powdered samples for EGA-CRDS were heated under vacuum without He flow, as He captured with CO₂ can interfere with isotopic measurements made using CRDS. The Hiden monitors mass 45 for CO₂ and at peak initiation, the manifold was opened and CO₂ collected via evacuated 1 Liter stainless steel cylinder as it was evolved from the sample. At the end of the run, the cylinder was backfilled with N₂ to a pressure of 2 Bar. The cylinder was closed and moved from the Hiden manifold to the CRDS manifold, which had been purged with N₂ and evacuated. Before introducing gas to the Picarro CRDS, the cylinder was opened into the manifold and gas flowed into a Teflon gas-sampling bag. When the pressure in the manifold equalized, the valve to the CRDS was opened and gas flowed from the bag into the CRDS at constant atmospheric pressure.

Results and Discussion: Seven lithologies were analyzed by EGA-CRDS (Fig. 2). Knorringfjell samples were cap carbonates associated with chemosynthetic organisms using methane as a carbon source when this fossil methane seep was active [2]. Sigurdfjell samples were carbonate crusts and cements associated with the basaltic vent complex very analogous to the carbonate globules in ALH84001 Martian meteorite [e.g., 3, 4].

At Knorringfjell, carbon isotopic data for the green (a) and black (b) lithologies indicate a biological



Figure 2. Left: Knorringfjell sample with a) black lithology, b) green lithology, and c) white lithology. Middle: Micrite (d) sample from Knorringfjell. Right: Sigurdfjell sample with e) external carbonate crust, f) internal carbonate, and g) carbonate/basalt interface cement.

source of carbon for carbonates. The heavier value for the white calcite layer (c) is consistent with mineral precipitation, possibly re-precipitation from dissolution of the other layers. The larger standard deviation came from diluting the sample slightly below the acceptable concentration (200 ppm) over which the instrument gives a linear response (this sample was 146 ppm).

Carbon isotopic analysis of micrite (d) from the same site yielded a $\delta^{13}\text{C}$ value of -19.1 ± 4.3 ‰. CO₂ capture and dilution resulted in 224 ppm CO₂ in N₂, just above the lower limit for instrument linearity, perhaps accounting for larger standard deviation than customary.

All $\delta^{13}\text{C}$ values from carbonates (e, f, g) at Sigurdfjell indicate mineral precipitation from inorganic carbon. The interface between the carbonate and basalt (g) had a larger standard deviation due to a slightly low sample concentration of ~ 198 ppm CO₂ in N₂. Carbon isotopic composition of basalt was not possible to obtain during this time due to lower concentrations of CO₂ during evolved gas analysis.

Table 1. $\delta^{13}\text{C}$ of AMASE 2010 samples by EGA-CRDS.

Sample	Lithology	$\delta^{13}\text{C}$ (‰) VPD
AM10-00005-06	Green, outside	-42.6 ± 1.2
AM10-00005-15	White	-11.4 ± 4.2
AM10-00005-23	Black, inside	-38.8 ± 1.1
AM10-00013-02	micrite	-19.1 ± 4.3
AM10-00027-02	carbonate/basalt	0.92 ± 3.9
AM10-00027-05	carbonate outside	0.71 ± 1.8
AM10-00027-08	internal carbonate	-2.8 ± 1.6

Implications: Two methodologies serving as proxies for the capabilities of the SAM instrument suite were employed in a Mars analog environment to measure the carbon isotopic composition of carbonates. The $\delta^{13}\text{C}$ values suggest a biological origin for carbonates from the “biotic” site, and an abiotic origin for carbonates from the “abiotic” site. The results from the coupling of EGA and CRDS indicate that laser spectroscopic measurements of CO₂ thermally evolved from heating of carbonate in a SAM-like pyrolysis oven is a valid method for measuring $\delta^{13}\text{C}$ of carbonates and can provide important information regarding the biogenicity of carbon in a Mars analog environment.

References: [1] Mahaffy P. R. (2008) *Space Sci Rev.*, 135, 255. [2] Nakrem, H. A. et al. (2010) NGF Abs. and Proc. of the Geo. Soc. of Norway [3] Treiman A. H. et al. (2002) *EPSL*, 204, 323. [4] Steele A. et al. (2005) *LPS XXXVI*, Abstract #2173.

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