https://ntrs.nasa.gov/search.jsp?R=20070009931 2019-08-30T00:28:00+00:00Z

A NEW METHOD FOR EVALUATING THE CARBON ISOTOPE CHARACTERISTICS OF CARBONATE FORMED UNDER CRYOGENIC CONDITIONS ANALOGOUS TO MARS.

P. B. Niles[1], R. A. Socki[1,2], P. L. Hredzak[3]; [1]Astromaterials Research and Exploration Science Office NASA Johnson Space Center, Houston, TX 77058 (paul.b.niles@nasa.gov); [2]Engineering Science Contract Group NASA Johnson Space Center [3]Department of Chemistry, Chatham College.

Introduction: The two upcoming robotic missions to Mars, Phoenix and MSL, will both have the capability of measuring the carbon isotopic composition of CO_2 in the martian atmosphere, as well as possible CO_2 trapped in carbonate minerals in the Martian soil. Results from orbital and landed missions now clearly indicate that no large scale deposits of carbonate materials exist at the surface. However, some results from orbital remote sensing have been interpreted to indicate that carbonate minerals are present as fine particles interspersed at low concentrations (~2%) in the martian dust [1].

One likely mechanism for the production of these carbonates is during the freezing of transient water near the surface. Large deposits of near surface ice [2] and photographic evidence for flowing water on the surface [3] suggest that transient melting and refreezing of H_2O is an active process on Mars. Any exposure of these fluids to the CO_2 rich atmosphere should allow the production of HCO_3^- solutions.

Carbonates are likely precipitates from these solutions during freezing as extensive CO_2 degassing, driven by the fluid's decreasing volume, drives CO_2 out. This rapid CO_2 degassing increases the pH of the solution and drives carbonate precipitation.

It has been shown in previous studies that this rapid CO_2 degassing also results in a kinetic isotopic fractionation where the CO_2 gas has a much lighter isotopic composition causing a large isotope enrichment of ^{13}C in the precipitated carbonate [4]. This kinetic isotope enrichment may be very common in the current martian environment, and may be a very important factor in understanding the very high $\delta^{13}C$ values of carbonates found in the martian meteorites [5-7]. However, while previous studies have succeeded in generally quantifying the magnitude of this effect, detailed studies of the consistency of this effect, and the freezing rates needed to produce it are needed to understand any carbon isotope analyses from carbonate minerals in the martian soil or dust.

This study demonstrates an innovative new method for measuring the isotopic composition of gas evolved from the freezing of carbonate solutions in real time, which allows for a much clearer view of the chemical processes involved. This method now sets the stage for detailed analysis of the chemical and isotopic mechanisms that produce cryogenic carbonates.

Methods: The method described here utilizes our new MAT 253 Isotope Ratio Mass Spectrometer installed at Johnson Space Center during the Fall of 2006. By running this instrument in continuous flow mode, we sample the headspace gas above a freezing solution continuously until the solution has completely frozen and CO_2 levels have dropped below our measurement threshold (Fig. 1).

Figure 1. A cartoon of the experimental setup with a cooled vial containing the solution on the left, the Gas Bench II in the middle and the MAT 253 IRMS on the right.

A calcium bicarbonate solution was created by dissolving 1 mmol of $CaCl_2 \bullet 2H_2O$ and 2 mmol of $NaHCO_3$ into 1 L of de-ionized water. A gas mixture of 0.3% CO_2 and 99.7% He was bubbled through this solution for 2 hours to form a solution with pH 7.5.

A 1.5 mL aliquot of this starting solution was injected into a sealed vacutainer vial which had been flushed with He. This vial was then placed into a slot in a stainless steel block that was cooled to -20°C. The headspace above the solution in the vial was sampled continuously through a sampling needle inserted through the rubber stopper. The CO_2, H_2O and He mixture of gases from the headspace traveled through capillary lines into a Gas Bench II where they were separated through a GC column, and injected into the MAT 253 mass spectrometer. This continuously measured the carbon isotope ratio of the CO_2 being evolved from the solution during the freezing event. In addition, measurements were also made of the $\delta^{13}C$ of the dissolved inorganic carbon (DIC) prior to freezing.

Results and Discussion: The $\delta^{13}C$ measurements of evolved CO_2 are shown in Figure 2. The initial gas that is evolved from the solution ($\delta^{13}C$= -20.5‰) prior to freezing is fractionated from the DIC ($\delta^{13}C$=-8.4) according to the expected equilibrium relationship [8]. However, this changes rapidly and the evolved gas becomes increasingly more depleted in ^{13}C. This is surprising because we would expect to see that the progressive removal of isotopically light CO_2 gas from

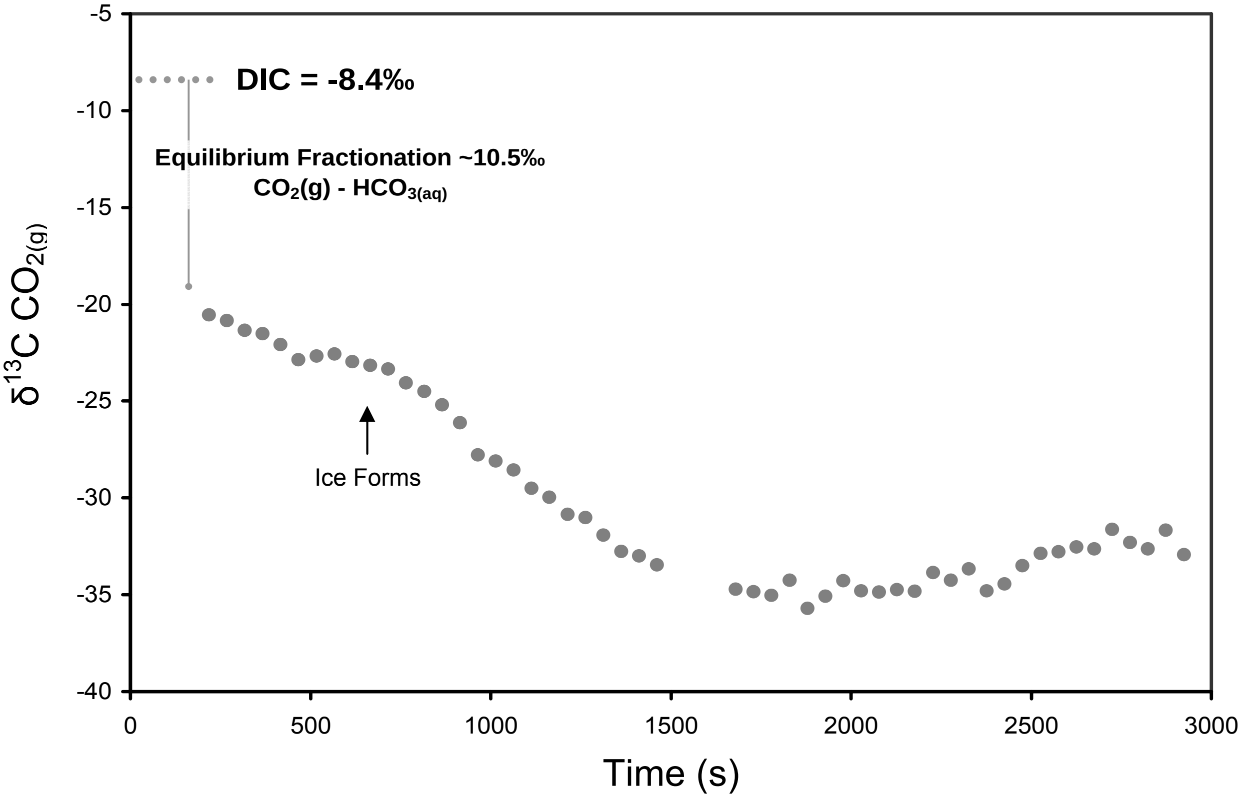

Figure 2. Points on the graph are $\delta^{13}C$ measurements of CO_2 degassed during the course of a freezing experiment. Ice was observed to form after ~600 s had elapsed in the experiment.

the system causes an enrichment of ^{13}C in the dissolved bicarbonate. This would in turn, result in an gradual increase in the $\delta^{13}C$ of the degassed CO_2 over time reflecting the increasing value of the source DIC. Rapidly formed solid carbonate carbonate typically shows very little isotope fractionation from DIC [9, 10], and thus would not affect this process.

Clearly, the $\delta^{13}C$ values of the degassed CO_2 are instead decreasing until the end of the experiment where they begin to rise somewhat (Fig. 2). Despite the increasing $\delta^{13}C$ of DIC, the $\delta^{13}C$ of the degassed CO_2 continues to decrease because the kinetic fractionation of carbon isotopes between DIC–$CO_{2(g)}$ is growing more rapidly [4]. When the $\delta^{13}C$ of the degassed CO_2 finally levels off at -35‰, the kinetic fractionation is at its largest. The magnitude of this kinetic fractionation effect has been quantified in previous studies to be as large as having a $1000*\ln\alpha= 31.2$ [4]. This means that the $\delta^{13}C$ difference between DIC and gaseous CO_2 is roughly 31‰. Our results agree with this previous study and suggest that this kinetic effect might be much larger since we expect that the DIC may have been enriched by as much as 10-20‰ based previous results. Detailed modeling of the carbon isotope composition of the DIC will be developed in future experiments.

Through real-time monitoring, the technique described here provides a significant enhancement over previous analysis methods, which are performed after the experiment has finished. Analyses done after freezing was complete in an identical experiment that was allowed to run without real-time monitoring yielded the $\delta^{13}C$ of the bulk outgassed CO_2 to be -25.8‰. This is about 9‰ greater than the most depleted gases observed in the real-time monitoring indicating that much larger variations are present on shorter time scales and real-time monitoring is needed to record these heterogeneities. This technique should prove extremely useful in determining the detailed isotopic fractionation effects and chemical processes that occur during cryogenic carbonate formation, and we also hope to apply these methods towards understanding cryogenic sulfate formation in the future.

References: (1.) J. L. Bandfield *et al.*, *Science* **301**, 1084 (Aug 22, 2003). (2.) W. C. Feldman *et al.*, *Science* **297**, 75 (Jul, 2002). (3.) M. C. Malin *et al.*, *Science* **314**, 1573 (December 8, 2006, 2006). (4.) I. D. Clark, B. Lauriol, *Chemical Geology* **102**, 217 (Dec 15, 1992). (5.) A. J. T. Jull *et al.*, *Meteoritics* **30**, 311 (1995). (6.) P. B. Niles *et al.*, *Geochimica Et Cosmochimica Acta* **69**, 2931 (2005/6/1, 2005). (7.) C. S. Romanek *et al.*, *Nature* **372**, 655 (1994). (8.) W. G. Mook *et al.*, *Earth and Planetary Science Letters* **22**, 169 (1974). (9.) J. V. Turner, *Geochimica Et Cosmochimica Acta* **46**, 1183 (1982). (10.) J. L. Dandurand *et al.*, *Chemical Geology* **36**, 299 (1982).