CRYOGENIC CARBONATE FORMATION ON MARS: CLUES FROM STABLE ISOTOPE VARIATIONS SEEN IN EXPERIMENTAL STUDIES. Richard A. Socki[1], Paul B. Niles[2], Qi Fu[3] and Everett K. Gibson, Jr.[2]; [1]ESCG and [2]KR, Astromaterials Research and Exploration Science, NASA/Johnson Space Center, Houston, TX 77058 (*richard.a.socki@nasa.gov)*, [3]Lunar and Planetary Institute, Houston, TX 77058.

Introduction:. Discoveries of large deposits of sedimentary materials on the planet Mars by landers and orbiters have confirmed the widely held hypothesis that water has played a crucial role in the development of the martian surface. Recent studies have indicated that both water ice [1] and liquid water [2] may have been present and in the case of water ice perhaps is still present on or near the surface of Mars. However, there remains much controversy about the prevailing atmospheric conditions and climate of Mars during its history and whether liquid water existed on the martian surface simply during discrete geological events or whether this water was present over relatively much longer geologic time periods. The recent identification of Ca-rich carbonate by the Phoenix lander [3] as well as its measurement of the isotopic composition of atmospheric CO_2 [4] has shown the importance of understanding the carbonates on Mars as an important sink of atmospheric carbon.

Freezing of bicarbonate-rich fluid results in the concentration of bicarbonate solutions, an increase in the pH, and subsequent precipitation of carbonate minerals. This process is similar to that which occurs during evaporation, and has also been shown to cause large kinetically driven carbon isotope fractionations as CO_2 degasses during the freezing process [5-7]. Cryogenic calcite forms when carbon dioxide degasses quickly from Ca-bicarbonate-rich water during freezing, a process that has been observed in arctic permafrost cave deposits [8] in lakebeds of the Dry Valleys of Antarctica [9], and in aufeis (river icings) from rivers of N.E. Alaska [10]. This phenomenon has been examined in detail by Clark and Lauriol, 1992 [5] when they analyzed the isotopic composition of bicarbonate-rich groundwater taken from caves in the karst region of Northern Yukon. They further showed that formation of cryogenic calcite is accompanied by non-equilibrium reaction kinetics that tends to enrich the isotopic composition of the product (calcite). We postulate that this freezing process could have been a common occurrence on the martian surface and/or the shallow subsurface resulting in the formation of carbonate minerals whose $\delta^{13}C$ composition is highly fractionated with respect to their parent bicarbonate solutions.

This work compliments that of our past experiments where we produced cryogenic calcite in open containers [11], as analogs for terrestrial aufeis formation [12], and as a means for evaluating the fractionation of ^{13}C in CO_2 during bicarbonate freezing [13]. Unlike our previous experiments in which carbonates were grown in ambient laboratory condition in open containers (atmospheric pressure and composition), this work attempts to quantify the amount of $\delta^{13}C$ enrichment possible in both fluids and secondary carbonates formed from freezing of bicarbonate fluids under martian-like atmospheric conditions. Morphologic textures of produced carbonates in these experiments are also examined under SEM in order to identify the effect that the cryogenic freezing process has on the mineral's mineralogy. Understanding the role of kinetic isotope fractionation during formation of carbonates under martian-like conditions will aid in our ability to quantify the isotopic composition of the carbonate sink furthering our ability to model the climate history of Mars.

Methods: Laboratory experiments were performed where calcium bicarbonate solutions were frozen under martian atmospheric conditions. Calcium bicarbonate solution was made by prolonged bubbling of pure carbon dioxide gas through a saturated solution of calcium hydroxide. Pressures were maintained inside the experimental vessel at ~6 mbars of a laboratory gas mix (Scott Mars Gas) that had the following composition: N_2 = 2.70%, Ar = 1.61%, CH_4 = 1.64% and CO_2 = balance, while simultaneously maintaining the temperature at -20°C. This was accomplished by circulating ethyl alcohol through the outer jacket of the Mars chamber. The pressure of the laboratory gas mix was maintained within +/- 0.1 mbars by adjusting a needle valve connected to the laboratory gas mix tank monitoring using a Varian senTorr vacuum pressure gauge controller. Another needle valve at the opposite end of the Mars chamber was connected to a vacuum line. Opening and closing the two needle valves precisely controlled the pressure inside the Mars chamber. Unlike our previous open container experimental set-up [11, 12], the Mars chamber experiments were designed to eliminate the effects of laboratory (terrestrial) atmosphere isotopic composition and ambient pressures. Bicarbonate fluid was prepared in the same fashion as our previous open container experiments. Once prepared ~10cc of this bicarbonate fluid was injected in to the Mars chamber via the septum port at the top of the chamber. Once the bicarbonate fluid in the chamber was completely frozen the valve to the laboratory gas mix was closed and the valve to the vacuum line was opened. This allowed the ice to sublimate similar to what would be expected on the surface of Mars, leaving solid carbonate at the bottom of the chamber. Once the solid carbonate was dried the Mars chamber was disconnected from the vacuum line and the solid carbonate precipitate was scraped from the chamber, oven dried and analyzed for ^{13}C composition.

Results: A total of five separate experiments were conducted in the Mars chamber using the technique outlined above. Data are summarized in Table 1. Carbon isotopes from both dissolved inorganic carbon (DIC) and solid carbonate were measured from each experiment. Oxygen isotopes from the carbonate and water used were also measured. The morphology of a typical cryogenically-produced calcium carbonate is shown in figure 1. The average $\delta^{13}C$ value of all DIC and solid carbonate analyses from the five experiments is -39.9‰ and -19.4‰, respectively. $\Delta_{(DIC-CARB)}$, the difference between the average values of the DIC and solid carbonate is 20.5‰ +/-4.5‰. The average $\delta^{18}O$ of water used was -6.8‰, with solid carbonate having $\delta^{18}O$ of 28.7‰.

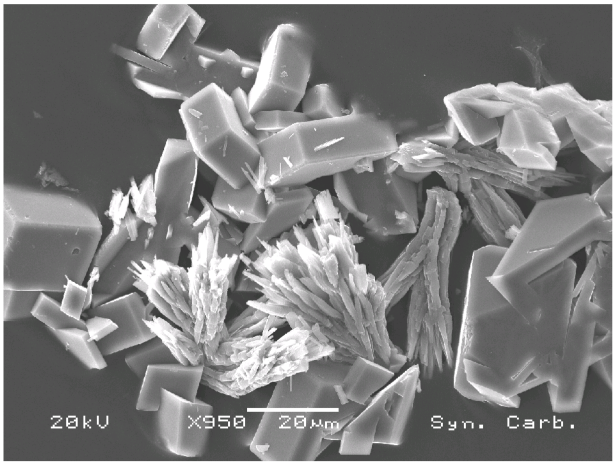

Figure 1. SEM photo of solid cryogenic carbonates produced from controlled laboratory freezing of Ca-rich bicarbonate fluid.

Our data indicate that the carbonates demonstrate enrichments in both carbon and oxygen isotopes beyond equilibrium values with average $\Delta_{(DIC-CARB)}$ values of ~20.5‰ which exceeds the expected equilibrium fractionation factor [$10^3 \ln \alpha = \sim 13‰$] at 0°C [14]. Oxygen isotopes showed a smaller enrichment with $\Delta_{(H2O-CARB)}$ values of ~35.5‰ slightly exceeding equilibrium fractionation factor of [$10^3 \ln \alpha = \sim 34‰$] at 0°C [15].

Implications for Mars: The discoveries of calcium carbonate by the Phoenix spacecraft [3] in the high latitude regions of Mars highlights the potential that carbonate formation occurs in the modern martian surface environment. This is also strengthened by the detection of low levels of carbonate present in the global dust [16]. This reveals a picture of carbonate formation more similar to what is observed in the Arctic [17] and the desert of the U.S. Southwest [18] environments rather than formation processes occurring in large bodies of water on Earth.

These experiments demonstrate that carbonates forming cryogenically under current martian conditions would be strongly enriched in ^{13}C beyond what is expected from equilibrium relationships. If carbonate formation has persisted over the prolonged cold dry history of Mars then we would expect the carbonate reservoir to reflect this ^{13}C-enriched signature.

These findings have implications for future efforts attempting to model the carbon cycle of Mars and climate evolution through time using the new carbon isotopic data returned from the Phoenix spacecraft as well as data soon to be returned from the MSL rover.

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	Carbonate		**DIC**	**H2O**	**Enrichment**	
Sample	**$\delta^{13}C$**	**$\delta^{18}O$**	**$\delta^{13}C$**	**$\delta^{18}O$**	**$\Delta^{13}C_{(DIC-CARB)}$**	**$\Delta^{18}O_{(H2O-CARB)}$**
MARS CRYO EXP 5-6-08	-22.66	25.43	-40.52	-6.93	17.86	32.36
MARS CRYO EXP 5-5-08	-20.32	26.97	-40.81	-6.92	20.49	33.90
MARS CRYO EXP 5-1-08	-11.90	28.08	-40.15	-6.63	28.25	34.71
MARS CRYO EXP 4-28-08	-22.00	32.14	-39.43	-6.76	17.43	38.91
MARS CRYO EXP 4-25-08	-20.11	30.89	-38.60	-6.62	18.50	37.50
Average Values	**-19.40**	**28.70**	**-39.90**	**-6.77**	**20.51**	**35.48**

Table 1. Data summary of Mars chamber cryogenic carbonate growth experiments. $\delta^{13}C$ data are reported relative to V-PDBstandard and $\delta^{18}O$ to V-SMOW standard. DIC=Dissolved Inorganic Carbon.