MARTIAN CRYOGENIC CARBONATE FORMATION: STABLE ISOTOPE VARIATIONS OBSERVED IN LABORATORY STUDIES.

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Introduction: The history of water on Mars is tied to the formation of carbonates through atmospheric CO_2 and its control of the climate history of the planet. Carbonate mineral formation under modern martian atmospheric conditions could be a critical factor in controlling the martian climate in a means similar to the rock weathering cycle on Earth. The combination of evidence for liquid water on the martian surface and cold surface conditions suggest fluid freezing could be very common on the surface of Mars. Cryogenic calcite forms easily from freezing solutions when carbon dioxide degasses quickly from Ca-bicarbonate-rich water, a process that has been observed in some terrestrial settings such as arctic permafrost cave deposits, lake beds of the Dry Valleys of Antarctica, and in aufeis (river icings) from rivers of N.E. Alaska. A series of laboratory experiments were conducted that simulated cryogenic carbonate formation on Mars in order to understand their isotopic systematics. The results indicate that carbonates grown under martian conditions show variable enrichments from starting bicarbonate fluids in both carbon and oxygen isotopes beyond equilibrium values.

Materials and Methods: Laboratory experiments were performed where calcium bicarbonate solutions were frozen under Mars-like conditions in a closed chamber (figure 1). The starting calcium bicarbonate solution was made by bubbling a carbon dioxide-rich laboratory gas mix (Scott Mars Gas) overnight through an over-saturated solution of reagent grade calcium hydroxide at room temperature. The Scott Mars Gas has the following composition: N2 = 2.70%, Ar = 1.61%, CH4 = 1.64% with CO2 as the balance. When conditions had reached the desired state (T = -20°C +/-0.1°C, P = ~6.0 +/-0.1 mbars) ~10cc of the Ca-bicarbonate fluid was injected into the chamber. Pressure control was actively maintained until the bicarbonate fluid in the chamber was completely frozen (~2 hrs), at which point the valve to the Scott Mars Gas was closed and the valve to the vacuum line was opened. We applied the vacuum at the end of the experiment in order to speed up removal of ice via sublimation, leaving solid carbonate at the bottom of the chamber. Since all of the carbonate precipitated during ice formation stage, additional pumping under vacuum conditions did not affect our experimental results. Once the solid carbonate appeared dry, the chamber was disconnected from the vacuum line and the solid carbonate precipitate was scraped from the chamber, oven dried at 50°C overnight and analyzed for its isotopic composition. Solid carbonate samples (fig. 2) were further analyzed using XRD and SEM in order to verify mineralogy and examine crystal morphology. $\delta^{13}C$ and $\delta^{18}O$ of solid calcium carbonate samples were analyzed via orthophosphoric acid extraction at 72°C in He-flushed exetainers. The $\delta^{13}C$ of dissolved inorganic carbon (DIC) was also measured by orthophosphoric acid extraction of the fluid in exetainers. The $\delta^{18}O$ of the bicarbonate solution was measured using the CO_2 equili-

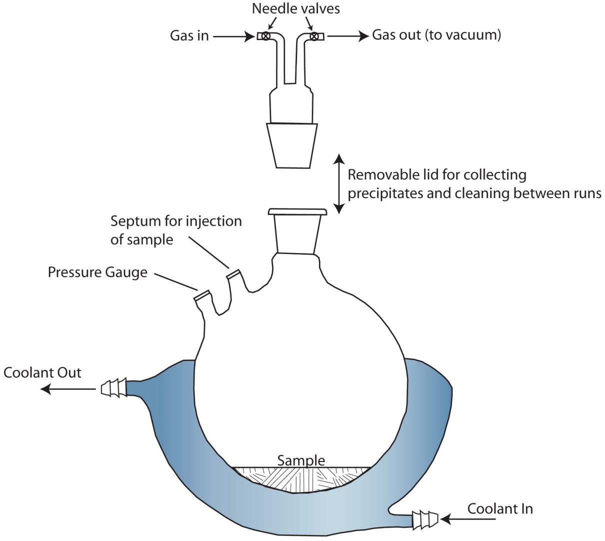


Figure 1. Mars environment chamber used for growing cryogenic carbonates. The ground-glass lid allows for cleaning the vessel between runs. Circulating chilled ethanol through the chamber's outer jacket controls temperature of the reaction. Pressure is maintained by adjusting both gas needle valves.

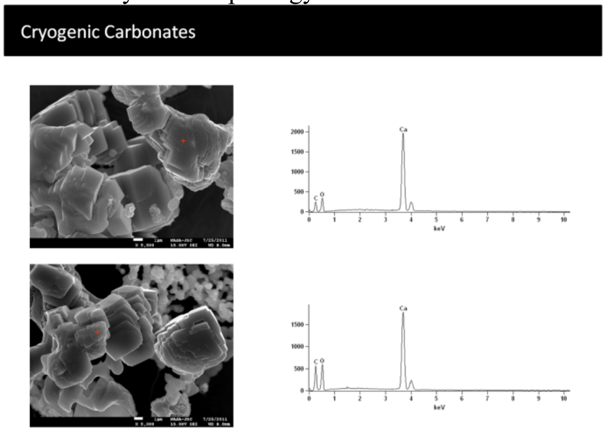
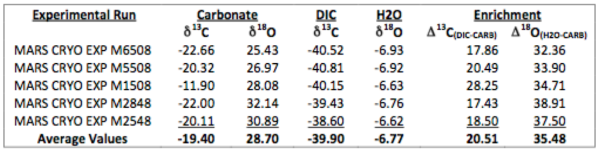


Figure 2. X-ray diffraction pattern (2a) and SEM photomicrograph (2b) of Ca-rich carbonates produced by freezing Ca-bicarbonate solutions under Mars-like conditions.

bration technique. All isotopic measurements were conducted on a Thermo Finnigan MAT 253 mass spectrometer via Gas Bench II.

Results and Discussion: A total of five separate experiments were conducted (Table 1). Average $\delta^{13}C$ values of the DIC and solid carbonate are -39.90‰ and -19.40‰ respectively. The difference between the average values of the DIC and solid carbonate ($\Delta_{\text{(DIC-CARB)}}$) is 20.51‰ +/-4.48‰. The average δ18O of the water in the bicarbonate solution was -6.77‰, with solid carbonate having δ18O of 28.70‰. The difference between the average values of the water and solid carbonate ($\Delta_{\text{(H2O-CARB)}}$) is +35.48‰ +/-2.68‰. Our data indicate that carbonates grown using the cryogenic technique described above show isotopic enrichments beyond values expected from equilibrium fractionations for both carbon isotopes ($10^3 \ln \alpha$ = ~13‰ at 0°C) [1] and to a lesser extent the oxygen isotopes ($10^3 \ln \alpha$ = ~34‰ at 0°C) [2]. XRD and SEM analyses show that experimental run products were composed of crystalline calcite rhombohedra with a typical diameter of ~5-10μm (fig. 2).



Experimental Run	Carbonate		DIC	H2O	Enrichment	
	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\Delta^{13}C_{(DIC-CARB)}$	$\Delta^{18}O_{(H2O-CARB)}$
MARS CRYO EXP M6508	-22.66	25.43	-40.52	-6.93	17.86	32.36
MARS CRYO EXP M5508	-20.32	26.97	-40.81	-6.92	20.49	33.90
MARS CRYO EXP M1508	-11.90	28.08	-40.15	-6.63	28.25	34.71
MARS CRYO EXP M2848	-22.00	32.14	-39.43	-6.76	17.43	38.91
MARS CRYO EXP M2548	-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 from Mars chamber cryogenic carbonate growth experiments. $\delta^{13}C$ relative to V-PDB and $\delta^{18}O$ to V-SMOW.

Discussion: Carbonates detected on Mars suggest that carbonate formation processes are likely to be as heterogeneous as they are on Earth, and it is unlikely that one single process will explain the formation of all carbonate on Mars. However, given the current geochemical conditions that prevail on the planet and the possibility that the martian climate may always have resembled these conditions [3], the potential importance of cryogenic carbonate formation cannot be ignored. Given the possibility for the presence of ephemeral liquid water [4-7], the process of cryogenic carbonate formation might be occurring on Mars today and/or in the recent past. Gullies, mostly within the walls of craters, south polar pits, and large martian valleys [8], may provide environments conducive to cryogenic carbonate formation. These gullies strongly suggest formation via processes associated with ephemeral liquid water [4,8-10]. Analogous to these martian features are carbonate deposits associated with terrestrial aufeis (river icings) commonly seen in springs and rivers of N.E, Alaska and Northern Yukon, which have been attributed to cryogenic carbonate mineralization processes [11, 12]. Results from our experiments clearly show that cryogenic processes can not only be an important mechanism for carbonate formation under martian conditions, but also demonstrate that a large kinetic isotope fractionation accompanies their formation that may provide a means for their identification. The large carbon isotopic enrichments observed in these experiments could be viewed as a lower limit since it is likely that martian systems would undergo extensive freeze-thaw cycles. If this occurs in a sedimentary environment away from the influence of atmospheric or microbial-produced CO_2, then very large isotope enrichments could be achieved as each freeze-thaw cycle would result in degassing of ^{12}C-rich CO_2, further enriching the solid phase in ^{13}C [13].

Summary and implications for Mars: The results of this study reveal that there are large variations in the isotopic enrichments of each experiment, even though these experiments were conducted under similar conditions. This degree of isotopic variability has also been observed in natural samples associated with terrestrial cryogenic environments [14] and could be a characteristic feature of carbonates precipitated under kinetic conditions. This observed variability likely results from the nature of carbonate precipitation in cryogenic or arid environments where there are multiple smaller episodes of carbonate precipitation driven by short duration wetting and/or melting events. These short duration kinetic effects result in isotope fractionations that may be similar to those observed in the experimental work described here, thereby producing variable isotopic composition of precipitated carbonates. Furthermore, large isotope variability has also been observed in the carbonates from martian meteorites [15]. The isotope variability seen in martian carbonates could also be the result of precipitation controlled by kinetics associated with cryogenic carbonate precipitation, similar to the cryogenic processes studied in the experiments reported here. In addition to cryogenically driven precipitation, kinetic processes affecting isotope composition could also accompany carbonate precipitation driven by rapid boiling and evaporation.

References: [1] Chacko T., et al. (1991) *GCA*, *55,* 2867. [2] Kim and O'Neil, Kim S.T. and O'Neil J.R. (1997) *GCA*, *61, 3461*. [3] Gaidos E. and Marion G. (2003) *JGR-Planets*, *108*. [4] McEwen A.S., et al. (2011) *Science*, *333, 740*. [5] Kahn R. (1985) *Icarus*, *62, 175*. [6] Hecht M.H. (2002) *Icarus*, *156, 373*. [7] Ingersoll A.P. (1970) *Science*, *168*, 972. [8] Malin M.C. and Edgett K.S. (2000) *Science*, *288*, 2330. [9] Heldmann J.L., et al. (2005) *JGR-Planets*, *110*. [10] Christensen P.R. (2003) *Nature*, *422*, 45. [11] Hall D.K., *Mineral Precipitation in North Slope River Icings*. 1980. Vol. 33. 1980. [12] Clark I.D. and Lauriol B. (1997) *Arctic and Alpine Research*, *29*. [13] Socki R.A., et al. (2001) *Lunar and Planetary Institute Conference Abstracts*, *32*, 2032. [14] Blake, W. (2005) Geografiska Annaler Series a-Physical Geography 87A, 175. [15] Niles P.B., et al. (2010) *Science*, *329*, 1334.