

**CRYOGENIC CALCITE – A MORPHOLOGIC AND ISOTOPIC ANALOG TO THE ALH84001 CARBONATES.** P.B. Niles<sup>1</sup>, L.A. Leshin<sup>1,2</sup>, R. A. Socki<sup>3</sup>, Y. Guan<sup>1</sup>, D.W. Ming<sup>3</sup>, and E.K. Gibson<sup>3</sup> <sup>1</sup>Department of Geological Sciences, Arizona State University (Tempe, AZ 85287-1404; pniles@asu.edu), <sup>2</sup>Center for Meteorite Studies, Arizona State University, <sup>3</sup>Astromaterials Research and Exploration Science Office, NASA Johnson Space Center.

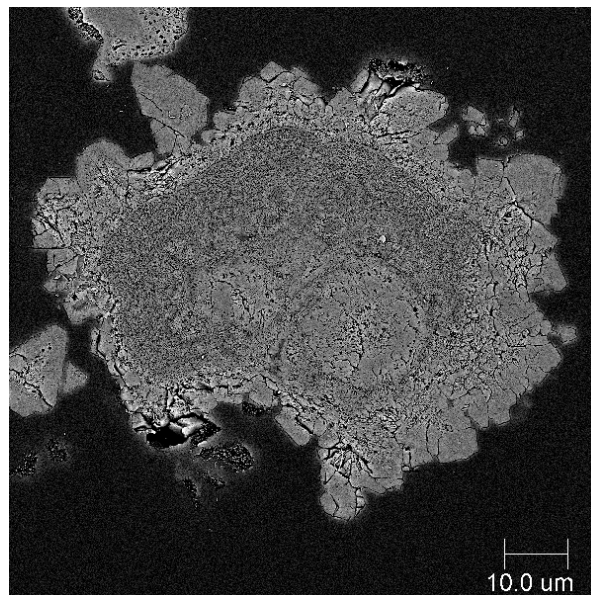
**Introduction:** Martian meteorite ALH84001 carbonates preserve large and variable microscale isotopic compositions [3-5], which in some way reflect their formation environment. These measurements show large variations (>20‰) in the carbon and oxygen isotopic compositions of the carbonates on a 10 – 20  $\mu\text{m}$  scale that are correlated with chemical composition [3-5]. However, the utilization of these data sets for interpreting the formation conditions of the carbonates is complex due to lack of suitable terrestrial analogs and the difficulty of modeling under non-equilibrium conditions. Thus, the mechanisms and processes are largely unknown that create and preserve large microscale isotopic variations in carbonate minerals.

Experimental tests of the possible environments and mechanisms that lead to large microscale isotopic variations can help address these concerns.

One possible mechanism for creating large carbon isotopic variations in carbonates involves the freezing of water. Carbonates precipitate during extensive  $\text{CO}_2$  degassing that occurs during the freezing process as the fluid's decreasing volume drives  $\text{CO}_2$  out. This rapid  $\text{CO}_2$  degassing results in a kinetic isotopic fractionation where the  $\text{CO}_2$  gas has a much lighter isotopic composition causing an enrichment of  $^{13}\text{C}$  in the remaining dissolved bicarbonate [6].

This study seeks to determine the suitability of cryogenically formed carbonates as analogs to ALH84001 carbonates. Specifically, our objective is to determine how accurately models using equilibrium fractionation factors approximate the isotopic compositions of cryogenically precipitated carbonates. This includes determining the accuracy of applying equilibrium fractionation factors during a kinetic process, and determining how isotopic variations in the fluid are preserved in microscale variations in the precipitated carbonates.

**Methods:** In order to control the experimental variables, the solutions contained only calcium. This simplifies the experiment and subsequent analysis of the products. A calcium bicarbonate solution was created by dissolving 4 mmols of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  into 200 mL of triple distilled water.  $\text{CO}_2$  gas was bubbled through this solution for 30 minutes, then 9.3 mL of 1M  $\text{NaHCO}_3$  solution was added to form a solution with pH 6.3. 100 mL of the prepared solution was added to a 150 mL narrow Pyrex beaker and placed in a freezer that maintained an approximate temperature



**Figure 1:** SEM backscatter electron image of a cryogenic carbonate globule. The globular shape and rim morphology are very similar to ALH84001 carbonates.

of  $-40^\circ\text{C}$  for 1 day. The precipitate was then isolated from the thawed solution by centrifugation, freeze dried, and a small portion was mounted in epoxy.

The thick section was polished and imaged using the JEOL JSM-IC 845 scanning electron microscope at ASU. The remaining powder was analyzed using a Siemens D5000 X-ray Diffractometer. Grains were analyzed using the Cameca IMS 6f at Arizona State University for their microscale carbon isotopic compositions. A 0.3 nA  $\text{Cs}^+$  beam was focused to a spot size of  $\sim 10 \mu\text{m}$  diameter using critical illumination. Secondary ions were collected at  $-9 \text{ kV}$  with typical count rates on calcite of  $\sim 2.8 \times 10^5 \text{ cps}$  for  $^{12}\text{C}$ . The average instrumental mass fractionation (IMF) on the calcite standard was  $-40.5\%$  with a standard deviation of 1.8‰ ( $1\sigma$ , 8 analyses). Uncertainties were calculated using a RMS method including individual analysis precision and the standard deviation of repeated analysis of the calcite standard.

**Results:** The freezing experiments formed carbonates with globular morphology (Fig. 1). This morphology is very similar in size and shape to the carbonate globules from ALH84001 [7]. X-ray powder diffraction on another fraction of the sample indicates that calcite is the only mineral present.

Two ion microprobe analyses were performed on a single globule. The innermost central zone had a  $\delta^{13}\text{C}_{\text{(PDB)}}$  of  $-31.9 \pm 2.4\text{‰}$  while the analysis of the outermost blocky zone revealed a  $\delta^{13}\text{C}_{\text{(PDB)}}$  of  $-19.4 \pm 2.1\text{‰}$  (Fig. 2).

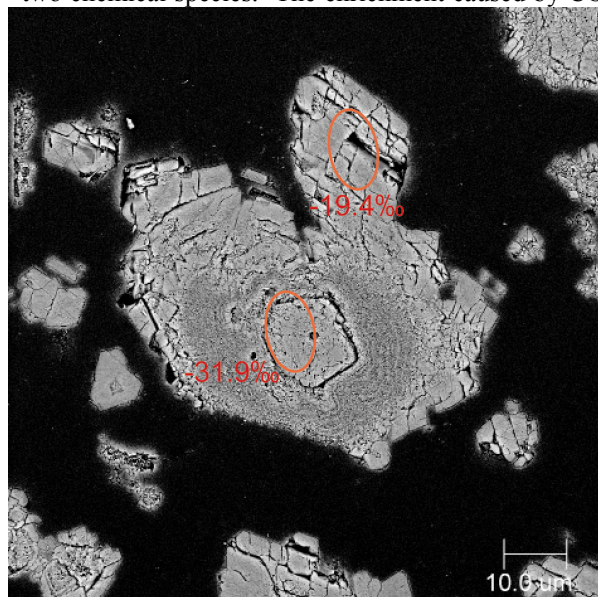
**Discussion:** The results show that cryogenic carbonate formation can produce carbonate globules similar in size and shape to the ALH84001 globules with significant microscale variations in  $\delta^{13}\text{C}$ . The pattern of enrichment in  $\delta^{13}\text{C}$  from core to rim is similar to that observed in ALH84001 carbonates but so far the magnitude of the enrichment is smaller in the experimental globules ( $\sim 12\text{‰}$ ) than the ALH84001 globules ( $\sim 20\text{‰}$ ) [5].

Modeling the observed isotopic variation is relatively straightforward. During the freezing of a bicarbonate solution  $\text{CO}_2$  solubility is decreased due to the removal of  $\text{H}_2\text{O}$  as ice [8].  $\text{CO}_2$  leaves the solution through the reaction:



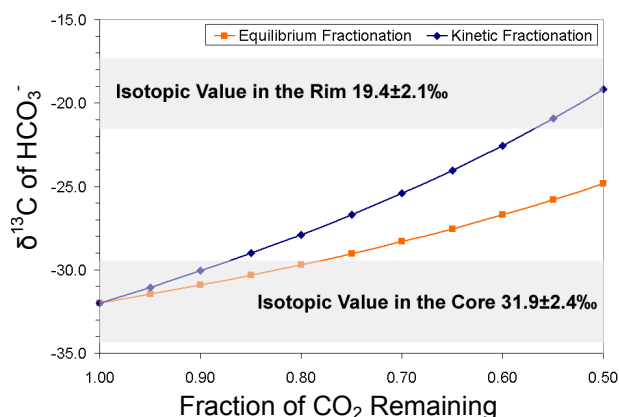
Thus equal molar amounts of  $\text{CO}_2$  gas and solid carbonate precipitate are created during this process. This is confirmed by measured yields from experiments performed by Clark and Lauriol [8], where molar amounts of  $\text{CO}_2$  and  $\text{CaCO}_3$  are relatively equal during the freezing of a bicarbonate solution.

The progressive removal of isotopically light  $\text{CO}_2$  gas from the system causes an enrichment of  $^{13}\text{C}$  in the dissolved bicarbonate. On the other hand calcite precipitation causes no significant change to the isotopic composition of the dissolved bicarbonate because there is very little carbon isotopic fractionation between the two chemical species. The enrichment caused by  $\text{CO}_2$



**Figure 2:** SEM backscatter electron image a cryogenic carbonate globule. Red ovals depict the location of carbon isotope analysis spots.

### Rayleigh Distillation during $\text{CO}_2$ Degassing



**Figure 3:** Modeled isotopic variation of dissolved bicarbonate during  $\text{CO}_2$  degassing. The top curve is calculated using a kinetic fractionation factor [1], while the bottom curve is calculated using an equilibrium fractionation factor [2]

degassing can be modeled using a Rayleigh distillation calculation, keeping in mind that roughly 50% of the dissolved bicarbonate is lost as  $\text{CO}_2$  gas and 50% is lost as calcite (Fig 3). This shows that a kinetic fractionation factor is more accurate in describing the isotopic compositions than an equilibrium fractionation factor.

**Conclusions:** 1.) Carbonate globules of similar size and shape to the ALH84001 carbonates can be formed under cryogenic conditions in the lab. 2.) The initial data presented here suggest that cryogenic carbonate formation can make and preserve micro scale carbon isotopic variations, although not as large as are observed in the ALH84001 carbonates. However, additional data are needed to confirm these results. 3.) Equilibrium relationships do not accurately describe the current data, although additional experiments are required to determine the effect of compositional changes in the fluid and how they are reflected in the precipitated carbonate.

#### References:

- [1] Stiller, M., J.S. Rounick, and S. Shasha (1985) *Nature* **316** 434-435.
- [2] Mook, W.G., Bommerso, Jc, and Staverma, Wh (1974) *Earth and Planetary Science Letters* **22** 169-176.
- [3] Valley, J.W., et al. (1997) *Science* **275** 1633-1638.
- [4] Leshin, L.A., et al. (1998) *Geochimica Et Cosmochimica Acta* **62** 3-13.
- [5] Niles, P.B., et al., in *Lunar and Planetary Science XXXIII*, CD-ROM #1655 (2002).
- [6] Michaelis, J., E. Usdowski, and G. Menschel (1985) *American Journal of Science* **285** 318-327.
- [7] Mittlefehldt, D.W. (1994) *Meteoritics* **29** 214-221.
- [8] Clark, I.D. and B. Lauriol (1992) *Chemical Geology* **102** 217-228.