

**CHEMICAL AND ISOTOPIC STUDY OF LAB-FORMED CARBONATES UNDER CRYOGENIC AND HYDROTHERMAL CONDITIONS.** 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.C. Golden<sup>3</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:** Aqueous environments on early Mars were probably relatively short-lived and localized, as evidenced by the lack of abundant secondary minerals detected by the TES instrument [1]. In order to better understand the aqueous history of early Mars we need to be able to interpret the evidence preserved in secondary minerals formed during these aqueous events.

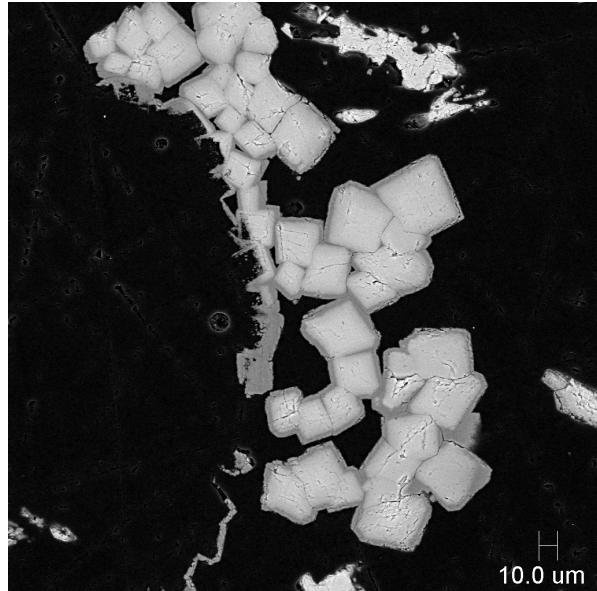
Carbonate minerals, in particular, are important secondary minerals for interpreting past aqueous environments as illustrated by the carbonates preserved in ALH84001[2, 3]. Carbonates formed in short-lived, dynamic aqueous events often preserve kinetic rather than equilibrium chemical and isotopic processes, and predicting the behavior of such systems is facilitated by empirical data.

Although many authors have suggested possible formation environments for carbonates on Mars, detailed analysis of the properties of carbonates likely to form under martian analog conditions remain scarce. Data from such experiments will be vital to interpreting analyses of martian meteorites, in situ data from future missions such as MSL, and data on returned martian samples. This laboratory study focuses on two potential martian carbonate formation environments that may have been significant during early martian history: a cryogenic and a hydrothermal environment. In the cryogenic environment, carbonates precipitate during the freezing of CO<sub>2</sub> rich water and subsequent extensive CO<sub>2</sub> degassing that occurs as the fluid's decreasing volume drives out CO<sub>2</sub> [4]. In the hydrothermal environment, carbonates precipitate during the heating of a CO<sub>2</sub> rich water which lowers the solubility of CO<sub>2</sub> and causes CO<sub>2</sub> degassing [5].

Experiments that mimic each of these environments have been run, and the carbonate run products have been analyzed for their chemical and isotopic compositions. The goal of this study is to identify the chemical and isotopic processes that occur in these environments and how these processes are recorded by the carbonates precipitated from each system.

**Methods:** The cryogenic experiments consisted of placing a 150mL calcium bicarbonate solution into a freezer that maintained an approximate temperature of -40°C for 1 day [6]. The precipitate was then isolated from the thawed solution by filtration.

The hydrothermal experiments consisted of placing 15mL of a Mg/Ca bicarbonate solution into a oven



**Figure 1:** SEM backscatter electron image of hydrothermal carbonate crystals. The darker areas reflect magnesite while the lighter areas are high Mg calcite.

which was warmed up to 150°C. The experiments were run for 5 days and quenched in a freezer (e.g. [7]). The precipitate was then isolated from the solution by filtration.

A portion of the cryogenic powder was reacted with 100% phosphoric acid and analyzed on the Finnigan Delta S dual inlet mass spectrometer at JSC. Another small portion from each of the experiments was mounted in epoxy for SEM and SIMS analysis.

The thick sections were polished and imaged using the JEOL JSM-IC 845 scanning electron microscope at ASU. The remaining powders were analyzed using a Siemens D5000 X-ray Diffractometer. Grains were analyzed using the Cameca IMS 6f at ASU for their microscale oxygen isotopic compositions. A Cs<sup>+</sup> beam was focused to a spot size of ~10 μm diameter using critical illumination. Secondary ions were collected at -9 kV using extreme energy filtering (EEF). Uncertainties were calculated using a RMS method including individual analysis precision and the standard deviation of repeated analysis of the calcite standard (all in 1σ).

**Results:** Isotopic analyses of the cryogenic carbonates using acid extraction of the powder resulted in a δ<sup>18</sup>O<sub>(SMOW)</sub> of +25.2±0.1‰. Ion microprobe analyses

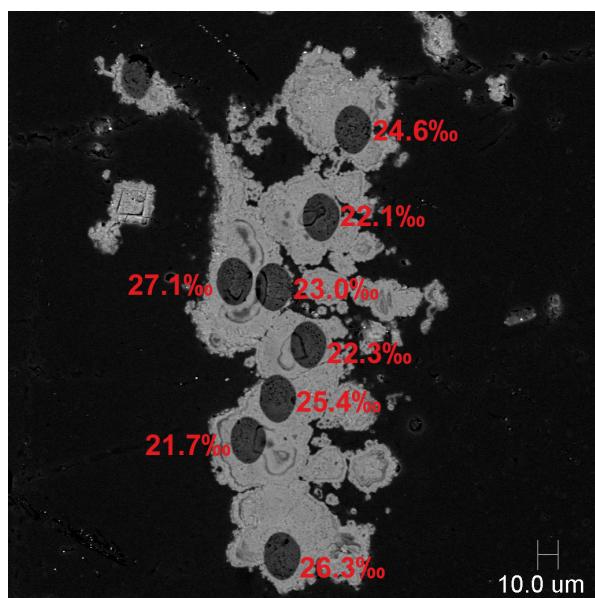
of the cryogenic carbonates yielded a range of oxygen isotopic values from  $\delta^{18}\text{O}_{(\text{SMOW})}$   $21.8\pm2.9\text{\textperthousand}$  to  $30.4\pm2.9\text{\textperthousand}$  (Fig 2), directly in line with the acid extraction values.

Hydrothermal carbonates formed from mixed Ca-Mg solutions show strong chemical zonation from Ca rich crystal cores to Mg rich crystal rims (Fig 1) similar to those produced by [7]. SIMS analyses revealed a variation in  $\delta^{18}\text{O}_{(\text{SMOW})}$  of  $+5.8\pm2.1\text{\textperthousand}$  to  $+16.8\pm2.2\text{\textperthousand}$ .

**Discussion:** These initial results show a small ( $>3\text{\textperthousand}$ ) oxygen isotopic variation in both environments. This variation is present on a microscale and is not detected in the simple one step acid-extraction experiments. Future stepped extraction analyses will be performed on the hydrothermal carbonates that will be a better comparison to the SIMS data.

The magnitude and direction of the isotopic variation is important in order to identify the dominant processes under each set of conditions. Initial indications are that the  $\delta^{18}\text{O}$  of the carbonate seems to be decreasing by a small amount under both experimental conditions. This remains a very tentative conclusion, and needs to be confirmed with more SIMS analyses.

If the  $\delta^{18}\text{O}$  is indeed decreasing under both conditions, then we can identify the dominant processes from the multiple processes that are capable of creating oxygen isotopic variations during these experiments. In the cryogenic experiments, water freezing dominates as it lowers the  $\delta^{18}\text{O}$  of the water by progressively removing more  $\delta^{18}\text{O}$  enriched ice from the system [8]. However another important process is  $\text{CO}_2$



**Figure 2:** SEM backscatter electron image of cryogenic carbonates. The dark circles are ion probe pits, and numbers are  $\delta^{18}\text{O}$  values for each analysis. Uncertainties are approx.  $\pm3\text{\textperthousand}$ .

degassing. If it occurs rapidly enough, the equilibrium between the dissolved bicarbonate and water won't be established, allowing for the removal of  $^{16}\text{O}$  rich  $\text{CO}_2$  gas from the system and the enrichment of the remaining bicarbonate[4].

In the hydrothermal experiments, the oxygen isotopic composition of the carbonates seem to be dominated by temperature change. As the temperature of the system rises carbonates become increasingly lower in  $\delta^{18}\text{O}$  as the fractionation decreases [9]. However,  $\text{CO}_2$  degassing may also be important causing the carbonate to become more enriched in  $^{18}\text{O}$ .

More measurements will help confirm the direction of the isotopic variation as well as the magnitude of the variations. Once the magnitude of the variations and other parameters are known, we will be able to more accurately model the processes and isotopic fractionations active under each condition.

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