

MODELING CHEMICAL AND ISOTOPIC VARIATIONS IN LAB FORMED HYDROTHERMAL CARBONATES. P.B. Niles¹, L.A. Leshin^{1,2}, D.C. Golden³, R.A. Socki³, Y. Guan¹, and D.W. Ming³ ¹Department of Geological Sciences, Arizona State University (Tempe, AZ 85287-1404; pniles@asu.edu), ²Center for Meteorite Studies, Arizona State University, ³Astromaterials Research and Exploration Science Office, NASA Johnson Space Center.

Introduction: Chemical and mineralogical data (e.g. [1]) from Mars suggest that the history of liquid water on the planet was more sporadic in nature than long-lived. The non-equilibrium chemical and isotopic compositions of the carbonates preserved in the martian meteorite ALH84001 are direct evidence of ancient secondary minerals that have not undergone significant diagenesis or stabilization processes typical of long-lived aqueous systems on Earth. Thus secondary minerals and sediments on Mars may primarily record the characteristics of the aqueous environment in which they formed without being significantly overprinted by subsequent diagenetic processes during burial.

Carbonate minerals, in particular, are important secondary minerals for interpreting past aqueous environments. The chemical and isotopic composition of carbonates formed in short-lived, dynamic, aqueous events are often dictated by kinetic rather than equilibrium processes, and it is necessary to use empirical data in predicting the behavior of such systems.

This laboratory study focuses on hydrothermal environments that may have been significant during martian history. In this environment, carbonates precipitate during the heating of a CO₂ rich water which lowers the solubility of CO₂ and causes CO₂ degassing [2]. This dynamic, non-equilibrium process may have been common in Mars' history.

Experiments that mimic this environment have been performed, 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 experiments consisted of placing 15mL of a Mg/Ca bicarbonate solution into an oven which was warmed up to 150°C. The experiments were run for 5 days and quenched in a freezer (e.g. [3]). The precipitate was then isolated from the solution by filtration. A small portion of precipitate from each experiment was mounted in epoxy for SEM and SIMS analysis. The solution was sampled before and after for Ca²⁺ and Mg²⁺ compositions using a GBC-903 atomic absorption spectrophotometer.

The polished thick sections were imaged using the JEOL JSM-IC 845 scanning electron microscope at

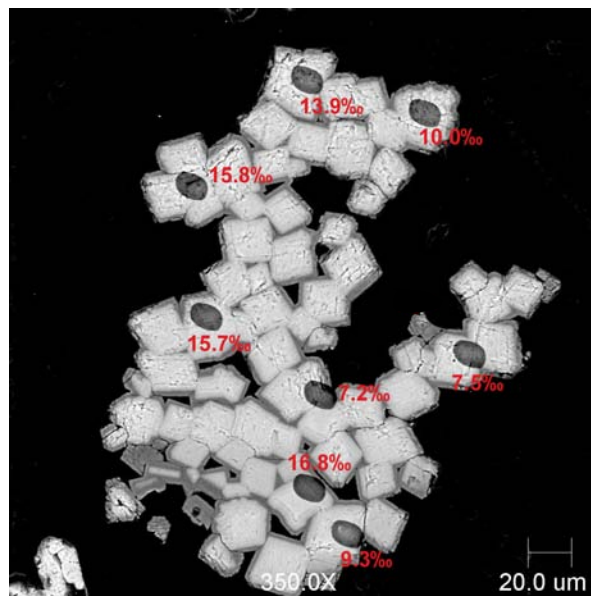


Figure 1: SEM backscatter electron image of hydrothermal carbonate crystals. The darker areas reflect magnesite while the lighter areas are high Mg calcite. Dark spots are SIMS analysis points labeled with $\delta^{18}\text{O}$ values.

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 oxygen isotopic compositions. A Cs⁺ 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: 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 [3]. The solutions sampled after the experiment showed the expected depletion in both Ca²⁺ and Mg²⁺ concentrations compared to the initial solutions. The reaction progress can be modeled by estimating relative abundances of Ca-rich carbonates and Mg-rich carbonates from SEM data (Fig. 1) and XRD data, and combining those data with changes in solution concentration (Fig. 2).

Isotopic composition of the carbonates measured by SIMS analyses revealed a variation in $\delta^{18}\text{O}_{(\text{SMOW})}$ of $+5.8\pm 2.1\%$ to $+16.8\pm 2.2\%$ (Fig. 1).

Discussion: The goal of this work is to pair the modeling and isotopic data to obtain a comprehensive picture of the processes that took place in the experiment. We expected that the magnesite rims on the carbonate crystals formed later than the calcite cores and would preserve a different isotopic signature from the cores. Contrary to our expectation, the initial SIMS oxygen isotope data are not obviously correlated with the chemical composition of the carbonates. If confirmed by stepped acid dissolution analyses that are currently underway, the oxygen isotope data may indicate that isotope fractionation is controlled by conditions in the micro-environment surrounding sites of precipitation rather than the conditions of the macro-environment. A similar micro-environmental effect may be indicated by the chemical modeling (Fig. 2) which shows that magnesite began to precipitate at a molar Mg/Ca ratio of ~ 6 . This Mg/Ca ratio is much lower than that observed by Jimenez-Lopez et al. [4] who observed that a molar Mg/Ca ratio of ~ 20 was required to precipitate magnesite at 70°C . Thus, local enhancements of Mg/Ca in particular micro-

environments may have been present in order to facilitate the formation of magnesite. However, at the maximum temperature (150°C) of this experiment, the Mg/Ca ratio necessary for magnesite formation is currently unknown.

An integrated chemical and isotopic model of the experimental conditions, has given us a more accurate picture of the dynamic environment under which zoned carbonates precipitate. Future work will seek to show how the processes of CO_2 degassing, temperature change, and carbonate precipitation act on the macro- and micro-environment.

References:

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Figure 2: Concentration of Mg^{2+} and Ca^{2+} cations in the solution during experiment. Initial and final concentrations are measured, while intermediate concentrations are modeled from mineralogy and chemistry of carbonates collected after the run.

