

AN EXPERIMENTAL STUDY OF KINETICALLY-DRIVEN PRECIPITATION OF Ca-Mg-Fe CARBONATES FROM SOLUTION: IMPLICATIONS FOR THE LOW-TEMPERATURE FORMATION OF CARBONATES IN MARTIAN METEORITE ALH84001. D.C. Golden¹, D. W. Ming², C. S. Schwandt³, R. V. Morris², S. V. Yang³ and G. E. Lofgren². ¹Dual Inc, Houston, TX 77058, d.c.golden1@jsc.nasa.gov, ²NASA JSC, Houston, TX 77058, and ³Lockheed Martin, Houston, TX 77058.

Introduction. ALH84001 is the oldest known Martian meteorite with a formation age of 4.5 by [1,2]. McKay et al. [3] claimed that the meteorite carried evidence for ancient Martian life and, since then, the meteorite and its carbonates have been the focus of an intense research effort. Carbonates in ALH84001 occur in several habits [4,5], are confined to cracks and vugs [4,6,7,8], and are compositionally zoned [6,9]. The carbonates have been variously described as “spheroidal aggregates of fine grained vug-filling structures” [6] and “thin pancakes” [3]. Nevertheless, all carbonate globules in ALH84001 are essentially identical in structure, internal stratigraphy, and composition [9,10].

The origin of the carbonate minerals in ALH84001 is controversial. The controversy revolves around the temperature and process of globule formation. The carbonates have been suggested to form as precipitates from multiple influxes of solution at low temperature [6], as products of biogenic activity [3], as crystallization products from CO₂-rich fluids at temperatures >650°C [7], as crystallization products from shock-melted material [11], and as precipitates from briny water percolating through meteorite fractures [12]. Carbonate formation temperatures in ALH84001 have been suggested to be anywhere from low (e.g., 25°C) to high (>650°C) temperatures.

The temperature of formation of carbonate globules in ALH84001 is crucial to the proponents of relict Martian life associated with the globules because life as we know is possible only under a narrow temperature regime (~0 to 120°C). Inference of the formation temperature of carbonate globules in ALH84001 has been difficult due to the paucity of terrestrial analog rocks for comparison [13] and the lack of experimental studies on carbonates of similar nature. Several of the proposed methods for the formation of the ALH84001 carbonates suggest a low-temperature, inorganic pathway; however, to our knowledge no experimental data has been presented to-date to confirm these claims. Therefore, it is imperative to determine if the carbonates that occur in ALH84001 can form at low-temperatures from an inorganic source.

Materials and Methods. Attempts were made to synthesize carbonate globules of the composition range magnesite-ankerite-siderite-calcite from supersaturated Ca-Mg-Fe carbonate solutions. The compo-

nents (Ca, Mg, Fe) were mixed as chlorides and, after adjusting the solution pH to 6.75 with (NH₄)₂CO₃, CO₂ was bubbled into the solution until saturation. Various molar ratios of Ca, Mg, and Fe were prepared as starting solutions, which were transferred to Teflon-lined stainless steel containers and sealed. Containers were then placed in ovens at various temperatures up to 150°C for 24 h. Additional experimental runs were conducted at room temperature (25°C). Reaction products were washed with DI H₂O to remove excess salts and then freeze-dried. The chemistry and mineralogy of solid phases were characterized by x-ray diffraction (XRD), transmission and scanning electron microscopy (TEM and SEM), electron microprobe analysis (EMPA), and Mössbauer spectroscopy.

Results and Discussion. Carbonate globules with ankerite-magnesite compositions were produced from Mg-rich Ca-Mg-Fe solutions at 150°C (Table 1). Chemical zonation of these carbonate globules are similar to the carbonate globules found in ALH84001 (Fig. 1). Calcium and Fe were zoned in the interior of synthetic globules and Mg was zoned around the globule rim. The ternary diagram for the carbonate globules that formed under these conditions (see Fig. 2) is very similar to the ternary diagram reported for ALH84001 [e.g.,4]. Formation of the carbonates from supersaturated solutions ensures rapid growth from a central nucleus. Apparently, Fe-Ca-rich carbonate precipitated first and acted as the nucleus for growth of the rest of the globule. The Mg-rich phase precipitated last once the solution was sufficiently depleted of other cations. This sequence is in concurrence with the saturation indices (SI) calculated for the test solutions using MINTQA2 ionic speciation program and the aqueous solid-solution phase diagram proposed for the CaO-MgO-FeO-CO₂-H₂O system [14].

Other experiments were conducted at 150°C in which the initial solution compositions were adjusted in a stepwise fashion in order to achieve ankerite and magnesite compositions in the range of those of ALH84001 (data not shown). Manganese was incorporated into the carbonate globules in relatively low levels and it followed a similar zonation trend as Fe, which was found to be the case with ALH84001 [3].

Experimental runs were conducted at room temperature (25°C) in an attempt to produce

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Table 1. Experimental conditions and products from synthesis of Ca-Mg-Fe carbonates.

Exper. #	Temp. °C	Cation Concentrations			Product Mineralogy (by XRD)
		Ca	Mg	Fe	
1	150	30	300	20	Ankerite, magnesite, magnetite
2	150	20	20	20	Ankerite-siderite, magnetite
3	25	25	20	20	Ankerite-siderite (poorly crystalline), calcite
4	25	30	300	30	Ankerite-siderite (poorly crystalline), calcite

ALH84001-like carbonates at temperatures more conducive for life. Although carbonate globules were produced from various starting compositions, no carbonate globules were produced that were similar in chemical composition, mineralogy, and chemical zonation to those found in ALH84001 (Table 1). Carbonates that formed from equimolar Ca, Mg, and Fe solution (each 20 mM) were initially poorly-crystalline Fe-carbonates (after 24 hr); however, if the solutions were allowed to stand for longer periods of time (96 h), globules of Mg-calcite formed. Similar trends were found in other experiments conducted at 25°C from varying starting compositions.

Carbonate globules similar in chemical zonation to carbonates formed at 150°C from Mg-rich solutions were also formed at 80 and 110°C from solutions with Mg-rich compositions. However, Mg incorporation was enhanced at 150°C over the 80 and 110°C runs. This may be due in part to the difficulty in synthesizing magnesite at temperatures under 100°C [15, 16].

Summary. Carbonate globules similar to those found in ALH84001 were synthesized from supersaturated, Mg-rich, Ca-Mg-Fe solutions at low temperatures (i.e., 150°C). These observations provide the first experimental data to support a low temperature, inorganic formation for the carbonates in ALH84001.

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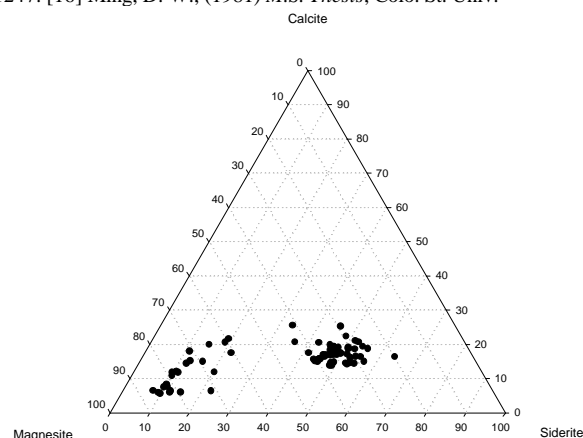


Figure 2. Ternary diagram (calcite-siderite-magnesite) for carbonates synthesized at 150°C from a CO₂-saturated, Ca (30 mM), Mg (300 mM), and Fe (20 mM) carbonate solution.

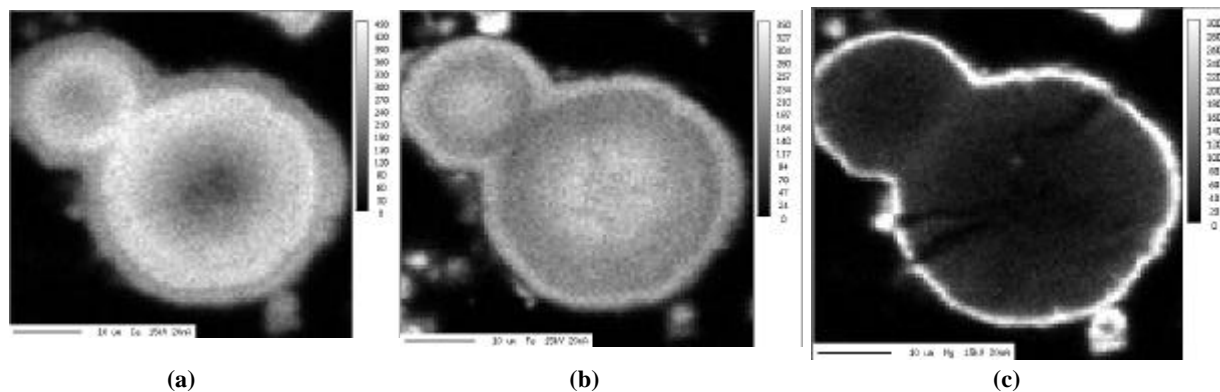


Figure 1. Elemental x-ray maps for carbonate globules synthesized at 150°C from a CO₂-saturated, Mg-rich Ca-Mg-Fe carbonate solution: (a) Ca distribution map (b) Fe distribution map, and (c) Mg distribution map.