MORPHOLOGICAL EVIDENCE FOR AN EXCLUSIVELY INORGANIC ORIGIN FOR MAGNETITE IN MARTIAN METEORITE ALH84001. D. C. Golden¹, D. W. Ming^{2*}, R. V. Morris², A. J. Brearley³, H. V. Lauer Jr.⁴, A. Treiman⁵, M. E. Zolensky², C. S. Schwandt⁴, G. E. Lofgren², and G. A. McKay², ¹Hernandez Engineering Inc., Houston, TX; ²ARES, NASA Johnson Space Center, Houston, TX; ³Dept. of Earth & Planetary Sciences, Univ. of New Mexico, Albuquerque, NM, ⁴Lockheed Martin, Houston, TX; ⁵Lunar & Planetary Institute, Houston, TX (*e-mail: <u>douglas.w.ming1@jsc.nasa.gov</u>).

Introduction: The origin of magnetite crystals in Martian Meteorite ALH84001 is the focus of a debate about the possibility of past (and present) life on Mars. McKay et al. [1] originally suggested that some of the magnetite crystals associated with carbonate globules in Martian Meteorite ALH84001 are biogenic in origin, because they are single magnetic domain, free of crystalline defects, chemically pure, and coexist with other metastable phases in apparent disequilibrium. Thomas-Keprta et al. [2,3] reported that a subpopulation of magnetite crystals (approx. 25%) associated with carbonate globules in ALH84001 and magnetite crystals produced by magnetotactic bacterial strain MV-1 have similar morphologies with crystal elongation along the [111] crystallographic axis that they describe as "truncated hexa-octahedral" ([111-THO]) magnetite. Along with several other properties, the [111]-THO morphology has been proposed to constitute a biomarker (i.e., formed only in biogenic processes), so that the presence of [111]-THO magnetite in ALH84001 may be evidence for past life on Mars.

Golden et al. [4,5] produced chemically zoned and sulfide-bearing carbonate globules analogous to those in ALH84001 by rapid (non-equilibrium) hydrothermal precipitation (at <150°C) from multiple fluxes of variable-composition Ca-Mg-Fe-CO₂-S-H₂O solutions. Brief heating of the precipitated globules produced magnetite and pyrrhotite within the globules by thermal decomposition of siderite and Fe sulfide, respectively [5]. The ankerite core and magnesite rim did not thermally decompose during this brief heating event. Magnetite crystals produced in the above manner had a narrow size distribution in the single domain to superparamagnetic range and were chemically pure, free of structural defects, and sometimes elongated in the [111] crystallographic axis.

In this study, we report and compare the threedimensional morphologies for magnetite crystals (1) produced inorganically by the thermal decomposition of Fe-rich carbonate, (2) extracted from carbonate globules in Martian Meteorite ALH84001, and (3) biogenically produced within the cells of magnetotactic bacterial strain MV-1.

Materials and Methods: Zoned carbonate globules with Fe-rich cores and Mg-rich (magnesite) outer zones were synthesized from solutions of Fe/Mg bicarbonates similar to the procedure of Golden et al. [6]. After synthesis the globules were placed in a 1-bar gas mixing furnace with $CO_2:CO = 95:5$. The temperature was ramped at 60°C/h to 550°C, held at temperature for 1 h. and then cooled at 200°C/h to ambient temperature. Magnetite crystals from the synthetic carbonate globules and from ALH84001 carbonate globules were extracted using acetic acid followed by thorough washing with deionized water. Magnetite crystals from MV-1 bacteria in magnetosomes were dispersed and washed in water by ultrasonic dispersion. Organic cellular materials were selectively oxidized [7,8] and magnetite crystals were washed again in cases where chemical analyses were performed. The extracted magnetite crystals from inorganic, ALH84001, and biogenic sources were mounted on carbon substrates on Cu grids. Magnetite particles were examined on a JEOL 2000FX TEM equipped with a Link system IV EDS or on a JEOL 2010 TEM equipped with a Gatan slow scan CCD camera. Magnetite 3-D shapes were deduced by observing 2-D images at different tilt angles [2,3,6], including views through [110] elongation ([110]_e) directions, where [111] $\{110\}_e \neq 0$. Projected 2-D images were compared to the simulated projections of 3-D polyhedral shapes generated using Jcrystal® software [9].

Results and Discussion: One drawback in determining 3-D shapes by tilt-image sequences of magnetite is that only certain directional views can be used to distinguish [111]-THO from other [111]-elongated morphologies (i.e., [111]-elongated cubo-octahedron ([111]-ECO) and [111]-elongated simple octahedron ([111]-ESO)). The view down the {110} axes closest to the [111] elongation axis of magnetite (for which $[111] \{110\} \neq 0$ provides a 2-D projection that can discriminate between [111]-THO and other [111]elongated morphologies ([111]-ECO and [111]-ESO). TEM photomicrographs for commonly observed [111]-elongated magnetite crystals oriented in this manner for each kind of sample are shown in Figure 1. The morphologies are differentiated by the shape of the corner denoted by the red arrows. Although all three [111]-elongated morphologies are found in all three samples, both ALH84001 and our inorganic samples have mostly [111]-elongated magnetite crystals with the [111]-ECO crystal morphology. In contrast, MV-1 has mostly [111]-THO magnetite crystals, in agreement with Clemett et al. [10].

These results show (1) that the morphology of the population of [111]-elongated magnetite crystals associated with the carbonate globules in Martian meteorite ALH84001 is reproduced by an inorganic process and (2) that the most common crystal morphology for biogenic MV-1 magnetite is morphologically different from both our inorganic laboratory products and the ALH84001 magnetite, which is in agreement with Buseck et al. [11]. It is not necessary to infer a probable biogenic origin for magnetite in ALH84001 as previously suggested by [1,2,3]. Furthermore, our inorganic synthesis method, the thermal decomposition of hydrothermally precipitated Fe-rich carbonate, is a process analogue for Mars. Namely, precipitation of carbonate globules from carbonate-rich hydrothermal solutions followed at some later time by a thermal

pulse, perhaps in association with impacts on the Martian surface.

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Figure 1: TEM views down the [110] axes closest to the [111] elongation axis of common morphological magnetite forms: (a) Inorganic magnetite crystals synthesized in the laboratory fit [111]-ECO model (best) and the [111]-THO model; (b) ALH84001 magnetite has a morphology analogous to synthetic inorganic magnetite, i.e., closely fits to a [111]-ECO model; and (c) magnetite from magnetotactic bacterial strain MV-1 with commonly observed {110} facets (arrow) conforming to a [111]-THO model [FFT = 2-D Fast Fourier Transformation of lattice fringe images].