INORGANIC FORMATION OF "TRUNCATED HEXA-OCTAHEDRAL" MAGNETITE: IMPLICATIONS FOR INORGANIC PROCESSES IN MARTIAN METEORITE ALH84001. D. C. Golden,[1] D. W. Ming,[2*] H. V. Lauer Jr.,[3] C. S. Schwandt[3], R. V. Morris,[2] G. E. Lofgren,[2] and G. A. McKay[2], [1]Hernandez Engineering Inc., Houston, TX, [2]NASA Johnson Space Center, Houston, TX, [3]Lockheed Martin, Houston, TX; [*]e-mail: douglas.w.ming1@jsc.nasa.gov

We report the first inorganic laboratory synthesis of a unique crystal morphology for magnetite that corresponds to magnetite produced by magnetotactic bacterial strain MV-1 and that is reported for some magnetite crystals in Martian meteorite ALH84001.

Introduction: McKay et al. and coworkers [1-3] suggested that a subpopulation (~27%) of the magnetite (Fe_3O_4) found in Martian meteorite ALH84001 might be biogenic (i.e., produced by magnetotactic bacteria), because crystals are single domain, free of structural defects, chemically pure, coexist with other metastable phases in apparent disequilibrium, and have a morphology (termed "truncated hexa-octahedral" or "THO" by [3]) that is the same as that produced by terrestrial magnetotactic bacterial strain MV-1. The "THO" shape is an octahedron elongated in one of the [111] directions, which introduces six faces of {110} (out of 12 possible dodecahedral faces) and truncated to various extents at the corners by cubic faces of {100} [3]. Brearley [4] suggested that single domain magnetite found in the rim regions of ALH84001 carbonate globules was produced by the thermal decomposition of Fe-rich carbonates. Based upon this idea, Golden et al. [5] synthesized ALH84001-like carbonate globules that contained single domain, chemically pure, and lattice defect free magnetite in globule rim regions. The magnetite was produced by precipitating zones of Fe-rich carbonate (siderite) from CO_2-rich fluids under hydrothermal conditions and then heating the carbonate globules (to ~470°C under 13.3 kPa CO_2 pressure) to simulate a thermal event, possibly initiated by an impact event to the meteorite's host rock. The three-dimensional (3-D) morphology of the inorganic magnetite was not studied in detail by [5].

The objective of this study was to determine 3-D morphologies of magnetite produced by thermal decomposition of Fe-rich carbonate. The approach was not to completely recreate ALH84001-like carbonate globules, but to determine if it is possible to produce magnetite with the unique "THO" morphology via siderite thermal decomposition.

Materials and Methods: Zoned carbonate globules with Fe-rich (siderite) cores and Mg-rich (magnesite) outer zones were synthesized in the laboratory using a modified method of [5]. Appropriate Fe and Mg chloride salts were dissolved in deoxygenated CO_2-saturated water. A $NaHCO_3$ pH buffer was added while CO_2 continuously passed through the solution; final solution concentrations were 0.04 mol/L $FeCl_2{\cdot}4H_2O$, x mol/L $MgCl_2{\cdot}6H_2O$ (x=0.004 to 0.12), and 0.20 mol/L $NaHCO_3$. Solution aliquots (15 mL) were transferred into 20-mL Teflon-lined hydrothermal pressure vessels, which were closed in a CO_2-atmosphere and transferred into an oven at 150°C for 7h. About 10-mg samples of hydrothermally produced siderite-magnesite globules were heated at 550ºC for 1h in gas-mixing furnaces with a CO_2:CO gas mixture (95:5) at ambient pressure. Magnetite grains were separated from carbonate globules containing magnetite, magnesite, and/or periclase by dissolving the magnesite (and periclase) in 20-40 μL of 20% acetic acid at 65ºC for 72h followed by H_2O washings (modified from [2]). Magnetite particles were examined on a JEOL 2000FX TEM equipped with a Link System IV EDS. Magnetite 3-D shapes were deduced by observing 2-D images of extracted magnetite grains at different tilt angles [2,3]. Crystallographic orientation was determined by selective area electron diffraction (SAED). Projected 2-D images of the magnetite shapes were compared to simulated projections of 3-D polyhedral shapes generated by JCrystal® software [6]. Size distribution (length vs. width) of magnetite particles was determined by digitizing low-magnification TEM micrographs and calculating the best fit of an ellipse to crystal contours [2,7].

Results and Discussion: Magnetite inorganically formed via thermal decomposition of siderite in our experiments is indistinguishable from magnetite reported by [3] as biogenic in origin and having the "THO" morphology. The crystal in Fig. 1a is rotated 66° around the tilt axis, which is in the plane of the paper. The {100} truncations at the corners of this crystal are clearly visible during the tilt sequence. This tilt sequence is very similar to the sequence shown for MV-1 magnetite in Fig. 2 of [3]. A second tilt series spanning 84º rotation for another crystal is shown in Figure 1b. The position at +7° is the view down the [001] zone axis clearly showing the (010) and (100) truncations at the corners. The SAED taken at +7° position corresponds to the [001] zone axis. Observed aspect ratios of the "THO" magnetite crystals synthesized in our experiments are similar to those reported for ALH84001 "THO" particles by [2]. For example, the mean particle length was 52±19 nm for

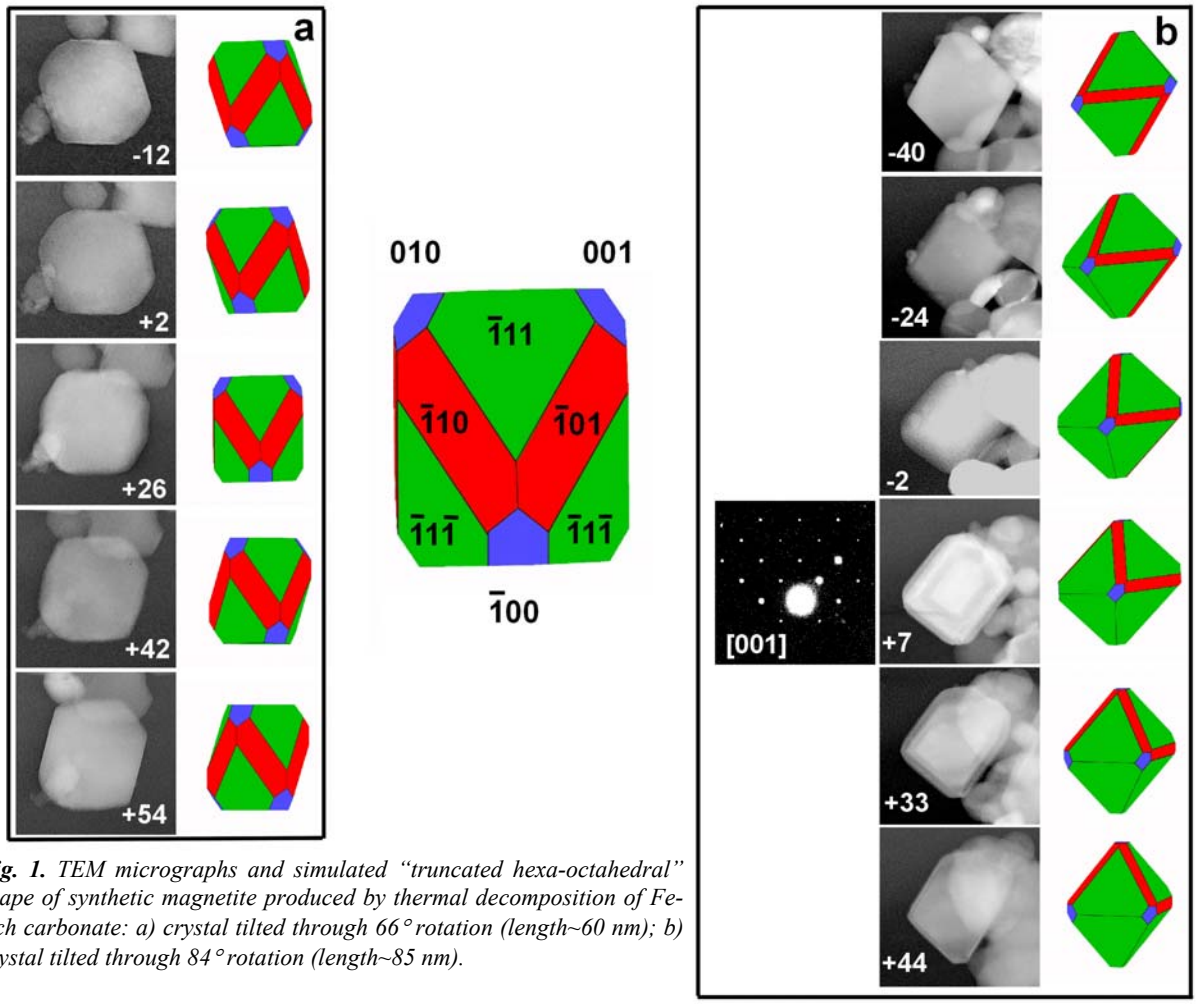

Fig. 1. *TEM micrographs and simulated "truncated hexa-octahedral" shape of synthetic magnetite produced by thermal decomposition of Fe-rich carbonate: a) crystal tilted through 66° rotation (length~60 nm); b) crystal tilted through 84° rotation (length~85 nm).*

"THO" magnetite produced from siderite decomposition (x=0.12 starting solution). Although the abundance of "THO" magnetite particles varied for different starting solutions, the abundance of "THO" magnetite produced from thermal decomposition of the above siderite sample was ~66% of the total magnetite; ~4% were other euhedral crystals (cubic, octahedral, 6-sided plates), ~27% were irregular shaped, ~2% were whiskers, and <1% were precipitated magnetite. Synthetically produced "THO" magnetite crystals were single domain, void of lattice defects, and elongated along the [111] crystallographic direction. Because some of these magnetite crystals were produced in Mg-rich solutions, undetectable to trace levels of Mg were found in association with the synthetic magnetite; this Mg may or may not be structural. Additional experiments are underway to determine trace element substitution into synthetic magnetite. Several factors appear to affect magnetite morphology, including decomposition temperature of Fe-rich carbonate and epitaxial and/or topotaxial relationships with thermally stable carbonate phases (e.g., magnesite) and the Fe-rich carbonate.

Conclusions: The thermal decomposition of siderite provides a suitable model for the formation of magnetite in the rim regions of ALH84001 carbonate globules. Magnetite produced by siderite decomposition in our laboratory experiments has the same morphology that has been reported for MV-1 and some ALH84001 magnetite by [2,3]. The inorganic formation of [111] elongated "THO" magnetite has far reaching implications for paleomagnetic interpretations of magnetite. The "THO" magnetite in ALH84001 may have formed by inorganic processes rather than by biologic processes as suggested by [1,2,3].

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