STATISTICAL ANALYSES COMPARING PRISMATIC MAGNETITE CRYSTALS IN THE ALH84001 CARBONATE GLOBULES WITH THOSE FROM THE TERRESTRIAL MAGNETOTACTIC BACTERIA STRAIN MV-1; Kathie L. Thomas-Keprta[1], Simon J. Clemett[1], Dennis A. Bazylinski[2], Joseph L. Kirschvink[3], David S. McKay[4], Susan J. Wentworth [1], H. Vali[5] and Everett K. Gibson[6]; [1]Lockheed Martin, Mail Code C-23, NASA/JSC, Houston, Tx, 77058, email: kthomas@ems.jsc.nasa.gov [2]Iowa State University, Dept. of Microbiology, 207 Science 1, Ames, IA 50011, [3]California Institute of Technology, Division of Geological and Planetary Sciences, 1200 E. California Blvd., Pasadena, CA 91125, NASA/JSC, SN, Houston, TX 77058, [4]NASA/JSC, SN4, Houston, TX 77058, [5]McGill University, Dept. of Earth and Planetary Sciences, 3450 University Street, Montreal, Quebec H3A2A7, Canada

McKay *et al.* [1] suggested that the fine-grained magnetite (Fe_3O_4) located within Fe-rich rims surrounding the carbonate globules in the Martian meteorite ALH84001 might be the fossil remains of Martian micro-organisms. This work is an extension of previous studies [e.g., 2-4]. Here we use rigorous mathematical modeling to compare a subpopulation of ALH84001 magnetites, called prismatic, with those produced by a common strain of terrestrial magnetotactic bacteria, MV-1. We find that this subset of the Martian magnetites appears to be statistically indistinguishable from those of MV-1. The implications of this resemblance as to their possible origin are discussed.

Methods ALH84001 and MV-1 magnetite crystals were extracted from carbonate globules and cells, respectively, and placed on transmission electron microscopy (TEM) grids and examined with a JEOL 2000 FX TEM [procedures described in 3]. Chemical analyses were performed using energy dispersive x-ray spectroscopy for 2,000 to 12,000 seconds. We determined magnetite crystal dimensions using the TEM at different tilt angles within the limits of our stage (±45°).

Results: General Morphology and Size Our previous work [3] showed that the extracted magnetite particles, found in clumps on the TEM grids, had a variety of morphologies including cuboidal-, rectangular-, teardrop-, irregular-, platy hexagonal-, and whisker- or rod-shaped. We examined 594 magnetite particles and identified three distinct subpopulations: irregular (389), prismatic (164), and whisker-like (41).

The irregular Fe_3O_4 crystals comprised 66% of the ALH84001 magnetite population and are characterized by low-symmetry shapes including cuboidal, teardrop, and other irregular forms not obviously belonging to either the prismatic or whisker-like groups.

The prismatic magnetites comprised 27% of the population and are defined by euhedral to slightly elongated crystals that have hexagonal cross-sections when viewed along the elongation axis [111 direction] and appear approximately rectangular when viewed along the other two perpendicular axes. The axial ratios (width/length) range between 0.4-0.9.

The whisker-like magnetites comprised 7% of the total. Axial ratios ranged from 0.1-0.3.

For comparison we studied size, shape, and axial ratios for 206 magnetite crystals from MV-1. The axial ratio range is from 0.5-1.0.

Results: Chemical Composition Previous results [4] showed that the prismatic ALH84001 magnetite crystals do not appear to contain any transition elements such as Ti, Cr, Mn, and Ni and are chemically pure at levels >few hundred ppm. Irregular and whisker-like crystals commonly contained Al and/or Cr. Biogenic magnetites were composed only of Fe and O with no Al or Cr. The ALH84001 prismatic magnetites and those from MV-1 are chemically indistinguishable.

Results: Statistical Analyses Figure 1 (A) shows the distribution of W/L ratios against lengths as observed by TEM for ALH84001 prismatic magnetites and magnetite extracted from MV-1. Overlaying the scatter plot are the theoretically calculated curves for superparamagnetic-to-single-domain and single-domain-to-multidomain transitions in pure magnetite [5]. Approximately 52% of the MV-1 magnetite crystals in our sample fell within the single-domain size, 16% in the transition range between single-domain and superparamagnetic, and 32% in the superparamagnetic range. 63% of the ALH84001 prismatic magnetites were in the single-domain size range, 20% were in the transition range, and 17% were in the superparamagnetic size range. Clearly both the ALH84001 prismatic and MV-1 biogenic magnetites cluster in the single-domain region, but significant scatter occurs extending into the superparamagnetic range.

Caution is required in drawing conclusions directly from Fig. 1 (A) because we must correct for geometric distortions that occur when we project a three-dimensional (3-D) object onto a two-dimensional (2-D) image plane as suggested to us by Buseck (Pers. Comm). TEM samples are analyzed by focusing an electron beam through the sample and onto an imaging plane. The outline of the observed image represents to the first order the shadow cast by the sample. Thus, it is difficult to identify crystal morphology and associated geometric properties from 2-D projections. In simple cases, however, we can deconvolve the 3-D geometry of a crystal and its W/L ratio from 2-D projection data. This procedure is valid provided the imaged crystals can all be represented by a single geometric shape and a sufficient number of samples exist to accurately approximate the “observed” W/L ratio distribution in the 2-D plane.

The most common projections of MV-1 at all tilt angles are hexagonal or rectangular shapes. There are only two 3-D geometric shapes capable of producing exclusively such 2-D projections: hexagonal prisms or cubes. Therefore we can assume that the “true” geometry of MV-1 biogenic magnetite is constrained to one of these geometries.

Like MV-1, TEM images of individual ALH84001 prismatic magnetites show either approximately hexagonal or cubic image projections suggesting the underlying 3-D crystal geometry to be represented by hexagonal prisms or cubes. Detailed TEM images of individual ALH84001 prismatic magnetites under incremental stage rotation bear a striking resemblance to MV-1 magnetites. In fact, it is not possible to distinguish between TEM images of MV-1 and ALH84001 prismatic magnetites. Therefore, we use the same geometric model for deconvolving the ALH84001 prismatic and MV-1 magnetites

An additional complexity of the model accounts for faceted ends that are rotationally offset from the facets at the other end by $\pi/3$ radians [6]. The resulting deconvolution reduces the scatter of Fig. 1 (A) to the tight patter of Fig. 1 (B). A similar deconvolution of data from ALH84001 prismatic magnetites also reduces the scatter of Fig. 1 (A) to the tight pattern in Fig. 1 (B). Not only does this show that MV-1 magnetites are nearly identical to ALH84001 prismatic magnetites, but also places most of the magnetites into the boundary region between the single domain and superparamagnetic fields. In the case of MV-1 biogenic magnetite the latter observation is consistent with the hypothesis that magnetotactic bacteria will grow magnetites in a controlled manner up to the point at which they cross the transition from superparamagnetic to single-domain behavior. **Mathematical formulas will be furnished at the conference and upon request.**

Conclusions Six specific properties of magnetite that increase the efficiency of its magnetization have evolved through the process of natural (Darwinian) selection, and they have been used successfully for nearly 20 years to identify the fossil remnants of bacterial magnetosomes (magnetofossils) in the sedimentary rock record on Earth [7]. The six criteria are: [1] single domain size and shape (including non-log normal size distribution); [2] chemical purity; [3] crystallographic perfection; [4] crystal morphology; [5] crystallographic elongation along the [111] axis; and [6] the presence of chains.

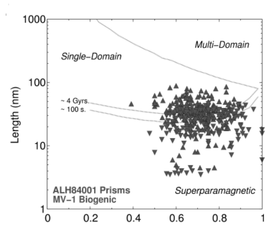
The carbonate globules in ALH 84001 are thought to be Martian in origin based on their isotopic composition and intimate association with the bulk matrix [e.g., 1,8]. The polycyclic aromatic hydrocarbons found in and around the carbonate rims have also been argued to be indigenous [1,9]. It seems likely therefore that the magnetites embedded within the carbonate matrix are also Martian. The magnetites that belong to the irregular and whisker-like subpopulations do not resemble those from bacteria strain MV-l; they each meet only one of the six criteria outlined above. Accordingly, their use as biomarkers does not seem justified. Terrestrial samples containing magnetite crystals in recent and ancient carbonates commonly show a mixture of both inorganic and biogenic magnetite [e.g., 10-12].

The similarity between the Martian prismatic magnetites and those from the terrestrial bacteria strain MV-1 is striking. This similarity might imply a common biogenic origin. We believe that additional Martian samples are necessary to establish this hypothesis. This work does demonstrate, however, that the Martian prismatic magnetites do meet the first five of the six criteria (our process of carbonate dissolution destroys the original spatial relationships) that must be satisfied for them to be interpreted as biomarkers.

References: [1] McKay D.S. *et al* (1996) *Science* **273**, 924. [2] Thomas-Keprta K.L. *et al* (1997) *LPSC* **XXVIII**, p. 1433. [3] Thomas-Keprta K.L. *et al*. (1998) *LPSC* **XXIX**, abst # 1494. [4] Thomas-Keprta K.L. *et al*. (1999) *LPSC* **XXX**, abst # 1856. [5] Butler R.F. and Banerjee S.K. (1975) *JGR* **80**, 4049 [6] Mann S. *et al* (1991) in Iron Biominerals, 21-49. [7] Kirschvink J.L. and Vali H. (1999) *LPSC* **XXX**, abst # 1681.[8] Treiman A. (1998) *Meteor. & Planet. Sci*. **33**, 753. [9] Clemett S.J. *et al* (1998) *Faraday Disc*. **109**, 417. [10] McNeill D.F. (1990) *JGR* **95**, 4363. [11] Hesse P.P. (1994) *Marine Geol*. **117**, 1. [12] Petersen N.et al (1986) *Nature* **320**, 611.

Figure 1. Size distribution of ALH84001 prismatic and MV-1 magnetites before (A) and after (B) deconvolution.

A



B