BIOGENIC MAGNETITE IN MARTAIN METEORITE ALH84001. Kathie L. Thomas-Keprta[1], Dennis Bazylinski[2], Susan J. Wentworth[1], David S. McKay[3], Joseph L. Kirschvink[4], Simon J. Clemett[5], Mary Sue Bell[1], D.C. Golden[6], and Everett K. Gibson Jr.[3], [1]Lockheed Martin, 2400 Nasa Rd. 1 Mail Code C-23, Houston, TX 77058 (email: kthomas@ems.jsc.nasa.gov), [2]Iowa State University, Dept. Microbiology, Immunology, and Preventive Medicine, 207 Science 1, Ames, IA 50011, [3]NASA/JSC, SN, Houston, TX 77058, [4] California Institute of Technology, Divison of Geological and Planetary Sciences, 1200 E. California Blvd., Pasadena, CA 91125, [5]MVA, Inc. 5500 Oakbrook Prwy. Suite 200, Norcross GA 30093, [6]DUAL Inc. Mail Code C-23, Jouston, TX 77058.

Introduction Fine-grained magnetite (Fe_3O_4) in martian meteorite ALH84001, generally < 200 nm in size, is located primarily in the rims that surround the carbonate globules [1,2]. There are two populations of ALH84001 magnetites, which are likely formed at low temperature by inorganic and biogenic processes. Nearly 27% of ALH84001 magnetite particles, also called elongated prisms, have characteristics which make them uniquely identifiable as biological precipitates.

Properties of Biogenic Magnetite At least five specific properties of magnetite which increase the efficiency of magnetization have evolved through the process of natural (Darwinian) selection and have been used successfully for nearly 20 years to identify the fossil remnants of bacterial magnetosomes (magnetofossils) in the sedimentary rock record on Earth [3]. We discuss these characteristics and relate them to a subpopulation of ALH84001 magnetite crystals.

(a) **single domain size and shape**: all tests of magnetosome crystals from living magnetotactic bacteria are in the single domain size range. These measuremements are done by comparing the physical size and shape requirements for single domain behavior [4] with the measured size and shape of the magnetosome crystals. Our measurements of ALH84001 magnetite crystals and those from bacteria strain MV-1 show that ~80% of each are in the single-domain size range.

(b) **chemical purity**: magnetite produced by magnetotactic bacteria is generally pure Fe_3O_4 and lacks minor or trace elements such as Ti, Cr, Mn, and Al. Magnetotactic bacteria seem to exclude these other elements in forming the growing magnetite crystals even though such elements are present in solution [5]. It has been well documented that naturally occurring magnetite is found in a wide variety of metamorphic and igneous rock types and commonly contains trace elements, particularly Ti, and exhibits isometric crystal habits [see references in 6]. The only literature examples of chemically-pure magnetite include nanometer-sized (<20 nm) magnetite in glass [7] and multidomain (50-1200 μm) magnetite in archean gneiss [8]. Magnetite in MV-1 and the elongated prismatic ALH84001 magnetite crystals were analyzed using energy dispersive spectrometry (EDS) for extended times (~2000-12,000 seconds) in order to detect trace elements. As a control, Ti, Mn, Fe, Co were readily detected using EDS at ~400-500 ppm in microtome (~100 nm thick) sections of a glass standard. ALH84001 elongated prisms do not appear to contain any transition elements such as Ti, Cr, Mn, and Ni and are chemically pure at levels > few hundred ppm; MV-1 crystals are also chemically pure at these levels.

(c) **crystallographic perfection**: high resolution TEM studies of magnetite crystals formed by magnetotactic bacteria show that they are free of internal crystal defects, with the minor exception of an occasional twin in the {111} plane [e.g., 9]. All of the ALH84001 elongated prismatic crystals were defect free; few twinned magnetites were found in the ALH84001 extracts and MV-1 magnetite crystals. Spiral screw dislocations have been reported in some of the ALH84001 whiskers [10] but have not been observed in elongated prismatic magnetites. Spiral screw dislocations were not found in any of the MV-1 biogenic magnetites.

(d) **magnetite chains**: virtually all magnetotactic organisms place their magnetite crystals in to linear chains. The total magnetic moment of the cell is maximized when the crystals are in a linear arrangement. Chains of collapsed magnetites are one indication that magnetotactic bacteria were present in terrestrial sediments [e.g., 11]. We examined magnetite grains extracted from ALH84001 carbonate globules so cannot infer inter-particle relationships however, magnetic chains of minerals in ALH84001 carbonates have been described by [12].

(e) **violation of crystal morphology**: the crystallographic arrangement of atoms in magnetite crystals produced by all magnetotactic bacteria is cubic; however, the crystal morphology is not the form (e.g., cubic, cubo-octahedral) typically associated with normal inorganic magnetic morphology. The magnetite crystals of MV-1 and likely biogenic ALH84001 magnetite crystals have elongated octahedral morphology. This morphology type is not cubic; only one of the four equivalent [111] directions is elongated and six of the twelve possible {110} faces are absent [13]. Presumably in the growth of biogenic, intracellular crystals, this morphology results from the magnetosome membrane blocking access to the elongate faces of the growing crystals. Several other examples of crystal morphology violations are known from the magnetotactic bacteria [13]. Elongation of crystals allows these biogenic magnetite crystals to achieve larger volumes and larger dipole moments without crossing into the multi-domain state as described in (a).

(f) **crystallographic direction of elongation of magnetite crystals**: typical MV-1 magnetite crystals, grown within the magnetosome membrane, are elongated in the [111] direction[e.g., 13]. The alignment of the magnetic moment along a magnetically "easy" [111] crystallographic direction (rather than a "hard" [100] direction) reduces the magnetostatic potential energy for the MV-1 crystals. The ALH84001 prismatic magnetite crystals are also elongated in the [111] direction.

Martian magnetite Previous work (procedures and results completely described in [2]) shows that magnetite typically range in size from ~10-200 nm. Cuboidal and irregular-shaped particles were most common; elongated prismatic particles comprised ~27% of the particles. Whisker/platelet-shaped grains which comprise ~6% of the total. ALH84001 elongated prismatic magnetites 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-shaped grains have variable compositions and commonly contain trace Al and/or Cr. The difference in the chemical composition of these two groups of magnetite indicates a distinct genesis for each group.

Martian magnetite formed by two different, low temperature processes We suggest that the ALH84001 magnetite formed by two different, low temperature mechanisms. None of the evidence supports high temperature *in situ* formation of any magnetite in the ALH84001 carbonate globules. Solid solution minerals such as MgO or CaO that would be produced by the incipient thermal decomposition of the carbonate globules have not been observed or reported. The presence of a variety of magnetite morphologies in ALH84001 carbonate globules is not surprising based on terrestrial examples that document the typical coexistence of biogenic and inorganic magnetite with diverse morphologies [e.g.,14-15].

The irregular ALH84001 magnetites are indistinguishable from some inorganic magnetite precipitates [e.g.,16] but are also indistinguishable from some kinds of extracellular magnetite made by bacteria [17]. The whisker ALH84001 magnetite could have formed at low temperature; the presence of screw dislocations and epitaxial relationship of these magnetites with carbonate are not indications of high temperature formation. Axial screw dislocations are known to form at low-temperatures, even in some biological minerals [18]. Epitaxy commonly occurs in minerals precipitated at low temperatures [e.g., 19]. The ALH84001 elongated prisms are morphologically (Fig. 1) and chemically identical to biogenic MV-1 magnetite crystals. The origin of the non-prismatic magnetite types in ALH84001 appears to be unrelated to the elongated prisms which, for reasons argued above, are completely consistent with the early presence of magnetotactic bacteria on Mars.

References: [1] McKay et al.,(1996) Science 273, 924. [2] Thomas-Keprta et al. (1997) LPSC XXIX, abst. #1494, LPI (CD-ROM). [3] Kirschvink and Vali (1999) LPSC XXX, abst. #1681. [4] Butler and Banerjee (1975) *J.Geophys. Res*. **80**, 4049 [5]Gorby et al. (1988) *J.Bacteriol*. **170**, 834. [6] Thomas-Keprta et al. (1999) LPSC XXX, abst. #1856 [7] Pick and Tauxe (1994) *Geophys. J. Int*. **119**, 116 [8] Benn et al. (1993) *Precamb. Res.* **63**, 59 [9] Vali et al (1987) *EPSL* **86**, 389 [10] Bradley (1998) *Meteoritics Planet. Sci.* **33**, 765 [11] McNeill and Kirschvink (1993) *J.Geophys. Res*. **98**, 7977 [12] Friedmann et al. (1998) Workshop LPI contribution #956, 14 [13] Mann et al. (1990) in *Iron biominerals*, 21-49[14] Belkaaloul and Aissaoni (1997) *Geophys. J. Int*. **130**, 411[15] Hounslow and Maher (1996) *Geophys. J. Int.* **124**, 57 [16] Nanophase Technology see www.nanophase.com/TEXT/PRODUCTS/IronOxide.html [17]Zhang et al. (1998) *Am. Min* **83**, 1409 [18] Wada (1968) *Bull. National Pearl Res. Lab* **13**, 1561[19] Dickerson (1993) *J. Sed.Pet.* **63,** 1.

Figure 1