

MULTIPLE ORIGINS OF MAGNETITE CRYSTALS IN ALH84001 CARBONATES; Kathie L. Thomas-Keprta¹, Simon J. Clemett¹, Christopher Romanek², Dennis A. Bazylinski³, Joseph L. Kirschvink⁴, David S. McKay⁵, Susan J. Wentworth¹, H. Vali⁶ and Everett K. Gibson⁴; ¹Lockheed Martin, Mail Code C-23, NASA/JSC, Houston, TX, 77058, email: kthomas@ems.jsc.nasa.gov, ²Savannah River Ecology Laboratory, Drawer E, University of Georgia, Aiken SC 29802 ³Iowa State University, Dept. of Microbiology, 207 Science 1, Ames, IA 50011, ⁴California Institute of Technology, Division of Geological and Planetary Sciences, 1200 E. California Blvd., Pasadena, CA 91125, ⁵NASA/JSC, SN, Houston, TX 77058, ⁶McGill University, Dept. of Earth and Planetary Sciences, 3450 University Street, Montreal, Quebec H3A2A7, Canada

Introduction: Analysis of the Martian meteorite Allan Hills 84001 has led McKay *et al.* [1] to suggest that primitive life existed on Mars approximately 4 billion years ago. One of the McKay *et al.* lines of evidence was the presence of nanometer-sized magnetite crystals within the meteorite, which could have been formed by redox chemistry known to be important in terrestrial microbial systems. Subsequently, Thomas-Keprta *et al.* [2,3] have argued that up to ~25% of these Martian magnetite crystals are in fact magnetofossils, which on Earth are formed exclusively by terrestrial magnetotactic bacteria. The remainder of ALH84001 magnetites may be products of processes including, but not limited to, precipitation from a fluid, thermal decomposition, or extracellular formation by dissimulatory Fe-reducing organisms. No single process, either inorganic or biogenic, can explain the full distribution of magnetites observed in ALH84001 carbonates. We propose that the origins of magnetites in ALH84001 can best be explained as the product of multiple processes.

ALH84001 History Unlike asteroidal meteorites that have experienced only one brief period of aqueous and thermal activity during their formation in the early Solar System, ALH84001 represents part of a dynamic and evolving planetary surface. Since its formation 4.5 Ga ago [4], it has experienced multiple shock events [5] and at least one, if not more, episodes of aqueous alteration [6]. Since more than one process has operated on the meteorite, it is logical that more than one process will be necessary to account for the diverse population of magnetites in ALH84001.

Distribution of ALH84001 Magnetites Carbonate globules in ALH84001 consist of an optically golden-colored core concentrically zoned in Ca, Mn, Fe, and Mg carbonate [e.g., 1] in which nanometer-sized magnetites (Fe₃O₄) are evenly distributed as a minor phase [1,2]. Surrounding the core is an inner and outer rim composed mainly of nanometer-sized magnetite crystals embedded in a Mg-rich FeCO₃ matrix [3] which are separated by a band of nearly pure Mg-carbonate.

Chemical and Physical Properties of ALH84001 Magnetites Magnetites in ALH84001 show a diverse range of chemical and physical properties. To a first order, we distinguish between biogenic and inorganic fractions.

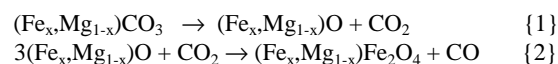
Biogenic Magnetite Approximately 25% of the ALH84001 magnetites display 5 of 6 properties that are uniquely characteristic of intracellularly produced biogenic magnetites from magnetotactic bacteria [2,3]. Both are single-domain, chemically pure, defect free, elongated along the [111] axis, and exhibit an unusual crystal habit we describe as truncated hexa-octahedral [3]. We determined the 3-D geometry of a

crystal mathematically from a series of 2-D projections taken at different orientations. The exterior shape of each 2-D projection is then expressed as series of intersecting planes that lie perpendicular to given projection plane. The 3-D geometry is then simply the convex hull [7], calculated by application of the Simplex algorithm, which is defined by the set of points corresponding to the intersections of these planes, subject to the constraints of the available crystallographic vectors. (Note: On Earth such truncated hexa-octahedral magnetites are only known to be produced by magnetotactic bacteria as no published reports of inorganic truncated hexa-octahedral magnetites are known.)

Abiotic Magnetite The remaining ~75% of the ALH84001 magnetites do not meet the criteria to be defined as biogenic. They show a variety of physical shapes that can be divided into irregular and regular. Irregular particles have low symmetry with generally poorly expressed crystal faces. Regular particles appear either as whiskers, plates, or equidimensional shapes. These magnetites can also be divided by their chemical composition. Some are chemically pure (stoichiometric Fe₃O₄) or contain minor to trace levels of Al and/or Cr.

Possible Origins of Abiotic Magnetite At the broadest level, magnetite can either be formed *in situ* in the carbonate by thermal decomposition or allochthonously (e.g., hydrothermal precipitation) and subsequently incorporated during the carbonate formation process. The thermal decomposition hypothesis has been proposed by both Brearley [8] and Golden *et al.* [9]. We suggest this cannot explain the presence of the *majority* of ALH84001 magnetites for the following reasons:

(1) Decomposition of (Fe,Mg)CO₃ under a CO₂ atmosphere proceeds via the reaction sequence:



Reaction {1} is mildly endothermic, while {2} is strongly exothermic. The exothermicity of {2} combined with poor thermal diffusion of carbonate would make it difficult to achieve only partial decomposition of carbonate.

(2) In ALH84001, the highest density of magnetite is found embedded in a (Fe_xMg_{1-x})CO₃ matrix [1,2]. Thermal decomposition of this matrix would lead to a mixed oxide phases (i.e., (Fe_xMg_{1-x})O & (Fe_xMg_{1-x})Fe₂O₄ as indicated in {1} & {2}, and *not* separate stoichiometrically pure phases (i.e., FeO, MgO, Fe₃O₄) [e.g., 10-12]. This is an inevitable consequence of the fact that Mg⁺² can replace Fe⁺² ions isomorphically in the lattices of both wüstite (FeO) and

magnetite (Fe_3O_4), i.e., a continuous series of solid solutions exist in both the FeO-MgO and $\text{Fe}_3\text{O}_4\text{-MgFe}_2\text{O}_4$ systems. As such the separation of phases would necessitate overcoming the significant combinatorial entropy associated with a mixed solid solution. This is analogous to the “entropy of mixing” in gases.

(3) A decrease in volume occurs in the conversion of FeCO_3 ($\rho=3.96 \text{ g/cm}^3$) to Fe_3O_4 ($\rho=5.15 \text{ g/cm}^3$) and while some magnetites appear associated with void space, the majority are not. Furthermore, for those that have voids, the void space is in general too large to be consistent with the ~20% reduction in volume on going from FeCO_3 to Fe_3O_4 . Our experimental data on carbonate decomposition are consistent with the anticipated 20% volume reduction and we do not observe the large ellipsoidal voids found in ALH84001, see Figure 1 (note: diffusion of CO_2 in carbonate is fast relative to magnetite formation and is virtually independent of grain size [13]).

(4) Thermal decomposition of pure, synthetic FeCO_3 was conducted by us under identical conditions to those of Golden *et al.* [9]. Complete conversion of carbonate to magnetite is observed, and the magnetite is characterized by poorly constrained, irregular shapes, see Figure 1. We suggest this to be a natural consequence of non-ideal growth conditions (i.e., chemical diffusion, surface kinetics, and heat conduction all influence crystal growth). In contrast, a significant fraction of ALH84001 magnetites show euhedral surfaces with symmetrical geometries characteristic of growth near thermodynamic equilibrium.

(5) Some magnetites in ALH84001 contain minor to trace concentrations of Al and/or Cr, and are found intimately mixed with chemically pure magnetites. Since neither Al or Cr can be incorporated into the carbonate structure, these magnetites must predate the surrounding carbonate and could not have formed by thermal decomposition.

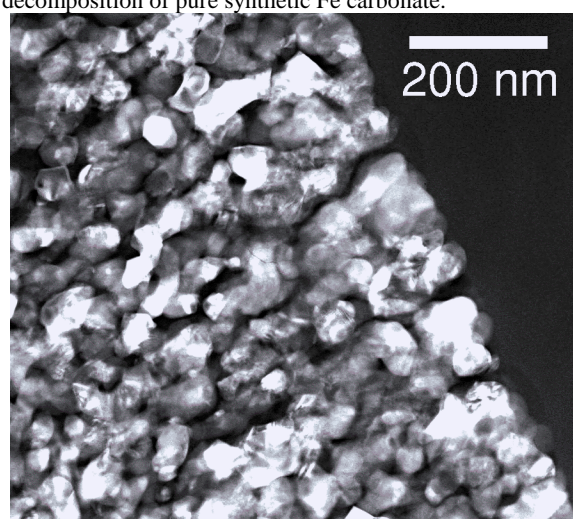
In light of these observations, we favor an allochthonous origin for the majority of ALH84001 inorganic magnetites. One hypothesis is the hydrothermal precipitation of magnetite from an Fe-rich fluid. Another hypothesis is the formation of magnetite by dissimilatory Fe-reducing organisms which facilitate mineral formation by creating external chemical environments suitable for extracellular magnetite precipitation [14]. For example, bacteria TOR-39 stimulates the production of superparamagnetic particles that are composed of a mixture of magnetite and Fe^{+3} hydroxide. At ~500 hours, the nuclei mature to nearly pure, single-domain magnetite [14].

Summary and Conclusions Magnetites in ALH84001 likely formed through biogenic and abiotic processes. In the case of the biogenic population we note that truncated hexa-octahedral magnetites on Earth are exclusively the product of biogenic activity -- no natural or synthetic inorganic process is known that could explain the observation of truncated hexa-octahedral magnetites in a terrestrial sample. Unless there is an unknown and unexplained inorganic process on

Mars, which is conspicuously absent on the Earth, we suggest that ALH84001 truncated hexa-octahedral magnetites formed by a mechanism similar to its terrestrial biogenic counterpart. In support of this, early Mars likely had free-standing bodies of liquid water [15], both organic [16] and inorganic carbon (e.g., atmospheric CO_2 [17]), energy sources, and likely possessed a planetary magnetic field [18] which would have been sufficient to support the growth of magnetotactic bacteria.

The origin of the majority of abiotic magnetites is not consistent with the thermal/shock decomposition process of FeCO_3 . A more tenable, although harder-to-prove hypothesis would involve the allochthonous accumulation of magnetites from hydrothermal fluids and incorporation during the growth of the carbonate.

Figure 1: Pure magnetite produced from the thermal decomposition of pure synthetic Fe carbonate.



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