

ON THE ORIGINS OF MAGNETITE IN MARTIAN METEORITE ALH84001. Kathie L. Thomas-Keprta¹, Susan J. Wentworth¹, David S. McKay², Dennis Bazylinski³, Mary Sue Bell¹, Christopher S. Romanek⁴, D.C. Golden⁵, and Everett K. Gibson Jr.², ¹Lockheed Martin, 2400 Nasa Rd. 1 Mail Code C-23, Houston, TX 77058 (email: kthomas@ems.jsc.nasa.gov), ²NASA/JSC, SN, Houston, TX 77058, ³Iowa State University, Dept. Microbiology, Immunology, and Preventive Medicine, 207 Science 1, Ames, IA 50011, ⁴SREL, University of Georgia, Aiken, SC 29802 ⁵DUAL, C-23, Houston, TX, 77058.

Introduction Magnetite (Fe_3O_4) in martian meteorite ALH84001 has been described as fine-grained, generally < 200 nm in size, and is located primarily in the rims that surround the carbonate globules [1,2]. We have suggested that a population of the magnetites may have been produced by low temperature, biogenic processes [2]. Fine-grained magnetites can be formed by inorganic (high and low temperature) or biogenic processes. We review those processes below and show that there are at least two populations of magnetite in ALH84001, produced at low temperatures, based on compositions, morphology, and size range.

Inorganic, high temperature Naturally occurring magnetite is found in a wide variety of metamorphic and igneous rock types and commonly contains trace elements, particularly Ti, exhibits isometric crystal habits [e.g., 3-4], and ranges in size from ~2 nm (in volcanic glasses [e.g., 5-6]) to millimeters (carbonates[7]). Nonequilibrium forms of magnetite, including elongated- and platelet-shaped, have also been described and range from ~200 nm to tens of micrometers in size and commonly contain Ti, Al, or V [e.g., 8,9]. In general, most magnetite in metamorphic and igneous rocks is not pure magnetite and typically contains other minor or trace elements [e.g., 3-4]. Fine-grain, single domain (SD) magnetite is found embedded in volcanic glasses and certain anorthositic-rich rocks [5,9]. Most SD magnetites from these regions contain some Ti. The only literature examples of chemically pure magnetite include nanometer-sized (<20 nm) magnetite in glass [10] and multidomain (50-1200 μm) magnetite in Archean gneiss [11].

Inorganic, low temperature Magnetite in soils may have formed by a variety of processes (e.g., detrital, authigenic). Equant SD magnetite crystals <10-100 nm commonly contain minor or trace Co, Ni, Zn, Cu, Mn, Si, Ca and Cr in widely varying amounts [12]. Magnetite has also been widely reported from carbonate rocks and sediments. Alteration of preexisting minerals (e.g. pyrite) result in botryoidal, spherical, framboidal, and irregular magnetite [e.g., 13, 14]. The interaction of oxidized iron minerals with hydrocarbons may produce magnetite with spherical or irregular shapes ranging in size from ~20 nm to several hundred micrometers [e.g., 15]. Fine-grained, SD

magnetite, superparamagnetic and multidomain magnetite are often found in carbonates. Some of the SD magnetite contains trace amounts of Mn or Ti with irregular morphologies and is believed to be formed by nonbiogenic processes. We note that there are ~140 occurrences of carbonates with embedded inorganic and biogenic magnetite described in the literature [e.g., 16-18].

Biogenic, low temperature It is not generally appreciated in the planetary science community that biogenic magnetite can be identified by the unusual, and in some cases, unique morphology, size range and composition of the magnetite crystals. Magnetite particles produced intracellularly by a variety of magnetotactic bacteria have diagnostic pure compositions (Fig.1), restricted size ranges (~20-150 nm in size), and distinctive morphologies. These criteria have been used extensively in the literature to characterize biogenic magnetite in terrestrial carbonates [e.g., 19-20]. Distinctive morphologies include those called parallelepipeds (hexagonal shape when viewed down [111] and rectangular shape when viewed along [111]) [e.g., 21]. Additionally, certain bacteria produce magnetite extracellularly and these crystals are morphologically identical to some inorganically produced magnetite [22]. Based on the criteria described above and the extensive literature on the characteristics of inorganic magnetite [3-11], we characterize ALH84001 magnetite into several subpopulations.

Martian magnetite Previous work (procedures and results completely described in [2]) shows that magnetite range in size from ~10-200 nm; one grain was ~500 nm in length. Cuboidal and irregular-shaped particles were most common; particles with parallelepiped-like morphology comprised ~ 25% of the particles. Whisker/platelet-shaped grains which comprise ~6% of the total, are also present in the carbonates [2]. For the first time, we have analyzed particles of different morphologies 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 at ~400-500 ppm in microtome thin sections ~100 nm thick of a glass standard using EDS. Parallelepiped-type magnetite do not appear to contain any transition elements

such as Ti, Cr, Mn, and Ni and are chemically pure at levels > few hundred PPM (Fig.1). Non-parallelipiped grains have variable compositions and commonly contain trace Al and/or Cr (Fig.1). 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. First, extensive literature containing descriptions of SD, chemically pure, parallelipiped-type magnetites invariably attribute this magnetite to a low temperature, biogenic origin. On the basis of this literature, as well as the lack of similar magnetite in nonbiogenic settings in other extensive literature, we interpret the SD, parallelipiped-type, ALH84001 magnetite to biogenic processes. Second, inorganic magnetites with euhedral/ subhedral/ irregular, and elongated shapes contain trace elements such as Cr and Al and can be formed at low temperatures. Euhedral Al-substituted magnetites up to 60 nm in size have been formed at ambient temperature [23]. Slightly substituted Cr-magnetites also form at low temperatures [24]. Unique elongated forms of magnetite (e.g., rods) have been reported from lab experiments at $T < 150$ °C [25]. The formation of low temperature terrestrial secondary (authigenic) magnetite requires a fluid that dissolves a precursor phase and crystallizes magnetite [14]. Given their small size, only extremely small quantities of fluid are necessary at any given time; the same fluids being utilized for dissolution, diffusion of components within a closed system, and crystallization of magnetite [14]. Iron used in the formation of authigenic magnetite may have come from any Fe-bearing minerals. In ALH84001, this Fe may have originated from pyrite. Most, if not all, pyrite surfaces in ALH84001 appear to be weathered or etched (Fig. 2) and exhibits compositional changes from a pure FeS_2 to one containing significantly more Fe and O. Chromium and Al may come from minor weathering of chromite. Further support for the formation of martian minerals (e.g., carbonate globules) at low temperatures is found in work by Zhang *et al* [26].

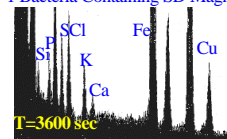
Conclusion We suggest that the ALH84001 meteorite contains evidence of inorganic, low temperature, aqueous processes and biogenic activity based on the morphology and chemistry of the magnetite, the association with carbonate which most likely also formed at low temperature [e.g., 26, 27], and the weathered appearance of other minerals [28] probably due to low temperature dissolution processes. *The origins of*

magnetite may be identified by examination of their morphology, chemical composition, and their relationship with other minerals [18].

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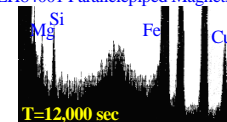
Figure 1

MV-1 Bacteria Containing SD Magnetite



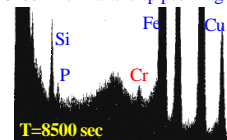
Elements Si,P,S,Cl
K, Ca are from residual cellular material. In all three spectra, Cu is from the TEM grids.

ALH84001 Parallelepiped Magnetite



Note lack of transition elements. Si and Mg are likely precipitates from acetic acid dissolved carbonates and slightly dissolved pyroxene. Al<100 PPM.

ALH84001 Non-Parallelepiped Magnetite



Note Cr peak (Cr~400 PPM). Si and P likely deposits from acetic acid used to dissolve carbonates. Pyroxene and phosphorus-rich minerals would be partly to completely dissolved in acetic acid.

Figure 2 Weathered Pyrite

