REEVALUATION OF THE "LIFE-ON-MARS" HYPOTHESIS: ALH84001 CARBONATE-MAGNETITE ASSEMBLAGES REVISITED K.L. Thomas-Keprta[1], S.J. Clemett[1], D.S. McKay[2], E.K. Gibson[2], S.J. Wentworth[1], FEI Corporation[3]; [1]ESCG at NASA/Johnson Space Center, Houston, TX 77058; [2]KR, ARES, NASA/Johnson Space Center, Houston, TX 77058; [3]FEI Company, Hillsboro, OR 97124 (kthomas@ems.jsc.nasa.gov)

Introduction The Mars meteorite ALH84001 is a sample of the ancient Martian surface with a crystallization age of 4.5 Ga. Internal cracks and fissures within this meteorite preserve evidence of early Martian hydrothermal activity in the form of carbonate-magnetite assemblages with disk-like appearance that are dated at 3.9 Ga. The mechanism(s) by which these disks formed has been a subject of considerable debate ever since the suggestion that biological processes could, in part, be responsible [1]. Subsequently, a number of alternative purely inorganic mechanisms have been advocated which all involve the partial thermal decomposition of sideritic carbonate to form magnetite (i.e., $FeCO_3 \rightarrow Fe_3O_4 + 2CO_2 + CO$). The main difference between these scenarios lies in the timescale over which decomposition is assumed to have occurred. Treiman [2] has advocated a slow thermal event in the Martian subsurface that lasted perhaps several hundred years (*"slow bake"*), while others [3-4] have invoked the nearly the nearly instantaneous heating and rapid cooling associated with final ejection even from the Martian regolith (*"fast bake"*).

In order to critically evaluate these inorganic mechanisms, we experimentally investigated the products of partial thermal decomposition of a natural sideritic carbonate over a range of heating regimes. Detailed TEM characterization of the samples was performed both before and after heating. These results were compared with those from multiple large-area (> 150 μm^2) TEM thin-sections of an ALH84001 carbonate disk and underlying orthopyroxene (Opx) which were extracted *in situ* from a 1-cm sized rock chip using focused ion beam (FIB) microscopy.

Methods *Heating Studies*: Samples of terrestrial sideritic carbonate from the Roxbury Iron Mine, Connecticut were selected as a good compositional analog to ALH84001 carbonate. These were heated to the point of decomposition under two heating regimes chosen to allow investigation of thermal decomposition products under conditions of both "*slow bake*" thermodynamic control and "*fast bake*" kinetic control. For "*slow bake*", the temperature was increased from ambient to 575°C at a rate of ~1 °C/min., held at this temperature for 24 hours, then allowed to cool slowly back to ambient. For "*fast bake*" a pulsed 10.6 μm CO_2 laser was used to rapidly heat samples at a rate ~10^8-10^9 °C/sec,

under vacuum, to a peak temperature of ~300-400 °C. Ultramicrotomed thin-sections of both the unheated and heated siderite were analyzed using TEM and EDX.

ALH84001 Carbonate: TEM sections of ALH84001 carbonate were obtained from a freshly exposed internal fracture surface of a rock fragment of ALH84001 from split ,386. After optical mapping of the fracture surface the rock chip was mounted, using C adhesive tape, on to a 1" SEM pin mount and sputter coated with 40 nm of Pt. An FEI dual beam Strata 237 Ga^+ FIB was then used to extract radial thin-sections from a carbonate disk embedded within the fracture surface. Because FIB thin-sections are subject to only minimal structural flexing the size of the thin-sections are considerably greater than has been previously possible using ultramicrotomy. In all, five thin-sections were obtained ranging up to 50×20 μm in size (Figure 1).

Results and Discussion *Heating Studies*: Roxbury siderite is an Fe-rich carbonate with a bulk composition of $[Fe_{0.84}Mg_{0.10}Mn_{0.04}Ca_{0.02}]CO_3$ [5], which is slightly more Fe-rich than the most sideritic carbonate that we have observed in the magnetite-rich rims of ALH84001 carbonate disks (~$[Fe_{0.73}Mg_{0.24}Mn_{0.01}Ca_{0.02}]CO_3$). EDX analysis of TEM thin-sections indicates compositional hetereogeneity extends from the mm down to sub-μm scale lengths. The Mg:Fe ratio shows at least a casual correlation with grain size, with fine grain component (< 100 nm) being typically Mg-poor (Fe:Mg > 20:1) while the coarse grained component (> 0.5 μm) is Mg-rich (Fe:Mg < 8:1). In either case however Mn and Ca concentrations tend to remain invarient.

Irrespective of the heating rate the product of thermal decomposition always resulted in a mixed cation oxide identified as a [Mg,Mn]-ferrite by selected area electron diffraction. Although the Mg content of individual ferrites varied from crystal to crystal the compositional range was similar to the variation of Mg in the original carbonate. This suggests the cause of the differences in Mg between ferrites is simply a reflection of the Mg content of the original carbonate. In contrast Mn concentrations were generally constant between ferrites.

ALH84001 Carbonate: TEM analysis of the FIB extracted thin-sections, in conjunction with narrow beam EDX, has provided the most comprehensive description of ALH84001 carbonates to date. A number of new observations are particularly pertinent to whether the carbonates have undergone partial thermal decomposition some of which are discussed outlined below. These observations relate either directly to the magnetites or provide constraints on the thermal history of the carbonate.

In the first case, by virtue of either composition or spatial location within the carbonate disk a fraction of magnetites are clearly not products of thermal decomposition. For example, chemically pure magnetite crystals are occasionally present within the magnesite band separating the inner and outer magnetite rich bands. Since this carbonate contains virtually no Fe its decomposition cannot produce magnetite. In other cases impure magnetites containing minor Cr are found in the core carbonate. Since Cr does not substitute into the trigonal (R-3c) carbonate structure, the Cr and by inference the magnetite in which it is present could not have been produced from decomposition of the carbonate matrix in which they are embedded. At a more subtle scale all the chemically pure magnetites observed *in situ* are in compositional disequilibrium with the surrounding carbonate, although re-equilibration of magnetite with surrounding carbonate (i.e., $2Fe_3O_4 + 3MgCO_3 \leftrightarrow 3MgFe_2O_4 + 2CO_2 + CO$) has been suggested as a mechanism for the formation of pure magnetite products from decomposition of [Mg,Mn]-rich siderite [2]. Careful thermodynamic reevaluation of this argument does not explain the absence of Mn and Mg in the magnetites we have observed within the ALH84001 carbonate.

In the latter case compositional mapping of the cation distribution within the carbonate indicate that the carbonate is not, as a whole, in thermodynamic equilibrium -- that is there is no evidence for phase separation into ankeritic-dolomitic and siderite-magnesite fractions. Furthermore concentric radial zoning profiles are preserved at a scale lengths of < 100 nm suggesting that thermally activated cation diffusion has not occurred to any significant degree.

Perhaps the most interesting findings, that have been enabled by the ability to examine large area thin-sections of carbonate in which both spatial and structural integrity have been maintained, is the presence of textural and chemical evidence for episodic exposure of the ALH84001 carbonate disks to fluids after formation. For example, magnetite-rich veins radiating inward toward the inner core, either horizontally from the inner magnetite rim, or vertically from the upper carbonate surface are observed to cross-cut entire car-

bonate sections. These veins are composed of magnetites intimately mixed with one or more amorphous silica phases and are texturally identical to the magnetite-rich rims, both of which show enrichments in Si 3× that of the core carbonate. We have also observed veins that cross-cut the core carbonate which are composed primarily of fine grained carbonates intermixed with an unidentified amorphous phase containing minor S. Finally, amorphous Fe-rich phases, likely ferrihydrite, are observed along fractures between crystal rhombs in the magnesite band.

Conclusions Results of experimental thermal decomposition studies of Roxbury siderite indicate that thermal decomposition of sideritic carbonate could not alone provide a viable mechanism to explain the presence of chemical pure magnetite in ALH84001 carbonate disks. Based on our new TEM results of ALH84001 carbonate thin-sections obtained using FIB extraction we instead argue for an allochthonous origin for the magnetites. That may be related to the textural and chemical evidence suggesting intermittent exposure of the carbonate to fluids with variable compositions after formation.
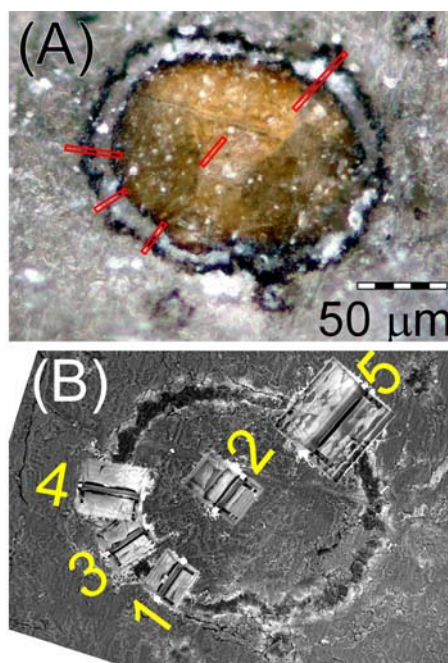

Figure 1: (A) Optical image of ALH84001 carbonate disk with location of extracted FIB thin-sections indicated in red; **(B)** SEM image of carbonate disk post extraction.

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