TEM ANALYSIS OF FINE-GRAINED MINERALS IN THE CARBONATE GLOBULES OF MARTIAN METEORITE ALH84001; Kathie L. Thomas-Keprta[1], Chris Romanek[2], Susan J. Wentworth[1], David S. McKay[3], Diana Fisler[4], D.C. Golden[5], and Everett K. Gibson[6]; [1]Lockheed Martin, Mail Code C-23, NASA/JSC, Houston, Tx, 77058, [2]SREL, University of Georgia, Aiken SC 29802, [3]NASA/JSC, SN, Houston, TX 77058, [4]Sandia National Laboratory, Alberquerque, NM [5]Dual, Inc., Mail Code C-23, NSA/JSC Houston, TX, 77058, [6]NASA/JSC, SN4, Houston, TX 77058

Because of the recent report of possible biogenic activity associated with the carbonate globules in the martian meteorite ALH84001[1], further discussion of the mineral phases associated with these carbonates is essential. In this study, we expand our original results using transmission electron microscopy (TEM) to describe the chemistry and mineralogy of fine-grained (nanometer-sized) regions in ALH-84001 carbonate globules and orthopyroxene (*opx*).

Carbonate globules have been previously described as being compositionally zoned (Ca-rich cores with alternating Fe-, Mg-rich bands) [*i.e.*,2-4] suggesting multiple episodes of carbonate deposition in fluids with changing chemistry at relatively low temperatures [5]. Other interpretations, however, suggest that these globules formed at high temperatures [6]. Examination of fine-grained regions in ALH84001 may reveal clues about the temperatures at which the carbonate globules and other fine-grained minerals were formed.

Methods A relatively flat region measuring 700 μm^2, which contained no fewer than 20 carbonate spheroids, was mapped with wavelength dispersive spectroscopy for major and minor elements using a Cameca SX 100 electron microprobe. In addition, three partial carbonate globules, removed from the meteorite with a W needle, were also chemically mapped. The globules were embedded in epoxy, thin sectioned using an ultramicrotome, and analyzed using a JEOL 2000 FX TEM [technique described in 7].

Chemical Mapping and TEM Analysis

Chemical Mapping: The mapped area contained ~ 20 carbonate globules ranging from ~20-250 µm in size. The core of the largest globule is composed of bands varying in Ca and Mn composition; the center of the core is (Ca, Mn)-rich surrounded by alternating bands, ~5-10 µm in width, of (Ca, Mn)-poor and (Ca, Mn)-rich carbonates. Away from the core, Ca, Mn banding is replaced by bands alternating in Mg- and Fe-rich carbonate. Black rims surrounding the globules are rich in Fe and S. The interior regions of the globules do not contain detectable S.

TEM Analysis of Black Rims: Thin (1-5 µm) Fe-rich rims, which surround the zoned carbonate centers, are composed of abundant fine-grained magnetite (Fe_3O_4) and minor pyrrhotite ($Fe\,S_{1-x}$, ~5 vol %) embedded in a lacy-looking, porous, fine-grained carbonate matrix. Individual magnetite grains range from ~10-100 nm in diameter; pyrrhotite grains range from ~20-100 nm in size. EDS and high resolution TEM data are consistent with magnetite and pyrrhotite. Magnetite crystals are cuboid, teardrop, and irregular in shape; individual crystals have well-preserved structures with no lattice defects and no minor or trace elements detected. Domains rich in pyrrhotite grains are distributed randomly within the rims; these grains have rounded to irregular shapes.

Additional elements observed in the EDS spectra of the black rims include Cl and P. Although not all of these elements are detected simultaneously, Cl and P can range up to ~1.0 wt.%.

Magnetites Within the Orange Carbonate Globules: Magnetites have been occasionally observed using tilting and darkfield techniques; in general they are similar in size and shape to those magnetites in the black rim [8]. We have one example of a chain of magnetites within one massive carbonate grain. These magnetites are ~10-100 nm in size and have cuboid shapes.

Three differences are evident between the texture and composition of the magnetites and carbonates in rims and the interior: (a) first, the concentration of magnetites in interior carbonates is far less than that observed in the black rims, (b) second, pyrrhotite grains that intimately coexist with the magnetites in the rim are absent within the globule interior, and (c) third, the interior carbonate is an intact, undissolved crystal unlike the fine-grained carbonate comprising the rim.

Phyllosilicates in ALH84001: Individual packets (nm-sized) and relatively large regions (~400 x 500 nm in size) of phyllosilicates have been observed in the *opx* regions found near some carbonate globules. The basal spacings measure 10-11 Å suggesting this is a smectite-type clay. This is the first documented report of hydrated minerals in ALH84001.

Formation of Fine-Grained Magnetites: A Controversy In ALH84001, Mg-Fe carbonate, magnetite, and pyrrhotite coexist at the micrometer scale, are clearly intergrown and constitute an assemblage; either low temperature processes including biogenic or high temperature inorganic processes could explain this assemblage.

Carbonate Globules: It has been suggested that the carbonate globules formed at T>650 °C [6]. Previous work by [5] and the present work of [9] suggest that ALH84001 carbonate globules were formed at low temperatures based on oxygen isotopes (<100 °C);

additional arguments against high temperature globule formation are given in [10]. At typical subsurface cooling rates of 1-1000 °C/my, the complex carbonate zoning patterns could not be preserved at temperatures >500 °C; the carbonates would be homogenized. This temperature is an *upper* limit for the preservation of the observed chemical zoning. Therefore, it is unlikely that the carbonate globules were formed at the high temperatures suggested by [6]. In addition, if the globules formed at lower temperatures, then the included magnetite would have also formed at the same temperatures.

Magnetite: Magnetite can be formed biogenically [*e.g.*, 11] or inorganically [*e.g.*, 12]. The nanometer-sized magnetites within the rim of the globules resemble magnetite crystals formed in low temperature environments by certain terrestrial bacteria (assimilatory and dissimilatory) based on crystal morphology, chemistry, and, crystal structure [*e.g.*, 11, 13]. The chain of single domain magnetites within a globule in ALH84001 resembles magnetosomes produced by magnetotactic bacteria [*e.g.*, 14]. In addition, the intimate coexistence of nanometer-sized magnetite and pyrrhotite favors a biogenic formation for these minerals [1]. Teardrop-shaped magnetites have only been observed to be formed to date by certain terrestrial bacteria [11]; we have observed magnetite with this shape in ALH84001 globules. A recent report suggests that whisker-like magnetites and twinned magnetite within ALH84001 carbonates are formed from high temperature environments such as fumaroles at 500-800 °C [15]; we submit two other possibilities here:

First, the formation temperatures of these rare whisker-shaped magnetites with screw dislocations are poorly constrained and it is unclear if similar growth mechanisms can produce magnetite at low temperature. Elongated magnetites have been observed from fumaroles; however, it is unknown if they are formed via screw dislocation growth. In addition, it is uncertain that carbonates with these complex zoning patterns and sulfides, could be produced from fumaroles; in general, magnesite decomposes at ~500 °C at atmospheric pressure (fumarole vents). Other expected volatile phases reported from fumaroles [16] have not been observed in ALH84001 globules [17]. However, it is known that certain terrestrial bacteria produce elongated, whisker-like magnetites with a length to width ratio of up to 10 [18] (Fig. 1) and other types of terrestrial bacteria can produce magnetite that is twinned [19]. Furthermore, bacteria-facilitated precipitation of magnetite and Fe-carbonate has been shown to occur at low temperatures [20].

Second, the whisker and twinned magnetites observed by [15] were found in coarse-grained carbonate without the presence of any Fe-sulfides; apparently they were not located within the carbonate globule rims that were described in [1]. In addition, it is unclear if these magnetites are located within carbonate globules or vein-filling carbonates within ALH84001.

All hypotheses regarding the formation of these minerals need to be rigorously evaluated because of the complex nature of the carbonate globules.

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Figure 1. Whisker-like magnetite produced by bacteria (arrows); the largest magnetite is ~300 nm long. Tear-drop crystals of magnetite, ~50 nm long, are also visible.