

A NON-BIOLOGICAL ORIGIN FOR THE NANOPHASE MAGNETITE GRAINS IN ALH84001: EXPERIMENTAL RESULTS Andrea M. Koziol¹ and Adrian J. Brearley², ¹Dept. of Geology, University of Dayton, Dayton, OH 45469-2364 USA; (koziol@notes.udayton.edu), ²Dept. of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA (brearley@unm.edu)

Introduction. Siderite (sid; FeCO_3) stability is controlled in part by O_2 and CO_2 fugacity. The carbonate globules found in martian meteorite ALH84001 and the ensuing discussions about their formation have increased interest in iron carbonate minerals.

Small magnetite (mt; Fe_3O_4) grains occur both in the core and rim of these globules. These grains have been interpreted as magnetotactic magnetite of biological origin [1, 2], vapor-phase condensation [3] or a by-product of siderite decarbonation due to a later shock reheating event [4]. In this experimental study, we formed small magnetite grains from sid-magnesite (magn; MgCO_3) carbonates similar in composition to those in ALH84001. Samples were held at elevated temperatures for a short time, to test the decarbonation hypothesis.

Experimental method. Experiments were performed at ambient O_2 fugacity and at reduced O_2 fugacity, close to graphite (gph)- CO_2 . Synthetic carbonates of compositions sid₁₀₀, sid₉₀magn₁₀, sid₆₀magn₄₀, sid₂₀magn₈₀, and sid₁₀magn₉₀ were used as starting materials. Samples were placed in Pt capsules, crimped, not sealed, and held at 470 °C for 5 minutes. Weight loss, if any, was measured before opening the capsules.

Experiments at reduced O_2 fugacity were performed in a nickel metal ashing crucible with tight-fitting lid. The crimped gold capsules were surrounded by fine-grained gph powder. It is estimated that conditions were probably at gph- CO buffer.

Transmission electron microscopy was carried out on the powders produced in the heating experiments. The powders were uncrushed and were deposited on copper TEM grids coated with a holey carbon film. A JEOL 2010 HRTEM operating at 200 kV was used for imaging and X-ray microanalysis was carried out *in situ* using an Oxford ISIS analytical system equipped with an ultrathin window EDS detector. Identification of the product phases in the experiments was performed using a combination of X-ray analysis and electron diffraction techniques.

Results. At both ambient and reduced O_2 fugacity, Sid₁₀₀ reacted extensively to magnetite, and the solid solution samples partially decarbonated. More Mg-rich compositions (i.e. sid₂₀magn₈₀) exhibited a lesser degree of reaction. An oxide spinel was present, but no hematite.

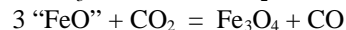
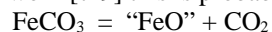
Remaining carbonate is somewhat variable in composition, as measured by EDS analysis. The unit cell volumes are reduced by 0.27% to 1.09% with progressively more contraction seen at more sid-rich starting compositions. Since magn-rich carbonates

have smaller volumes, this could indicate preferential decarbonation of the siderite component of the carbonate. Oxide spinel formed in these experiments exhibited contraction of unit cell, as shown by the 311 reflection. The contraction was dependent on carbonate composition, with more contraction noted at more Mg-rich starting compositions.

TEM images of experimental products show clumps of magnetite crystals forming pseudomorphs after rhombohedral carbonate grains (fig. 1). Some carbonate grains appear untouched. This is seen at both ambient and reduced O_2 fugacity. These pseudomorphic replacements consist of porous aggregates of myriad magnetite grains that are in random orientations. There is no evidence of any preferred crystallographic orientation of the grains.

Individual magnetite grains are in a restricted size range of 10 to 20 nm in size with good crystal shapes (fig. 2). There appear to be no defects or obvious twinning. Shape, size, and size distribution of magnetite grains are *very similar* to those seen in ALH84001 [2, 5]. The grains are also very similar to those produced by heating hydrothermally precipitated carbonates [6]. We have not observed grains with a whisker morphology as described by [3], supporting the hypothesis that grains with this morphology formed by a different means.

Magnetite or Magnesioferrite? Is magnetite, Fe_3O_4 , forming, or is magnesioferrite, MgFe_2O_4 , forming in these experiments? Qualitative data indicate little to no Mg in the oxide phase. The remaining carbonate material has a smaller unit cell, indicating a more magnesian composition. The exact reaction taking place has not yet been confirmed, but based on previous work [7-9] this is probably a two-step process:



However, no FeO was detected. Previous studies indicate that the first step proceeds rapidly.

It appears that the iron component of the carbonate is breaking down preferentially. Images of oxide grains produced are in figures 1 and 2.

Carbonate and Magnetite Assemblages in ALH84001: What does it mean? Could these phases be associated with each other because the magnetite grains formed after a short thermal pulse? Can the specific magnetite grain sizes and shapes be reproduced in the laboratory? This is important because Thomas-Keprta et al. (2000) (see also [5]) inferred a biologic origin because a subset of magnetites extracted from Martian meteorite ALH84001 exhibited 5 out of 6 criteria used to identify a biosignature. These

are: 1. single magnetic domain size and restricted length to width ratios; 2. chemical purity (no Mg present); 3. intact crystal lattice, with very rare defects or twinning present; 4. unusual crystal morphology of an elongated hexagonal prism; 5. elongation of crystal along [111] direction. The sixth criterion, magnetites arranged in chains of particles, was not observed.

We have not examined the detailed morphological characteristics of the magnetite grains, because this requires disaggregation of the pseudomorphs. Our initial findings suggest that rounded, subrounded, and equant crystal morphologies *similar* to those observed by [2, 5] are present within a very restricted size range. Well-developed facets are present on many grains (fig.2). The complex overlap of magnetite grains in the clumps makes detailed morphological analysis difficult. Further study would elucidate the characteristics of the grains.

Conclusions. I have attempted to recreate the mineralogy and textures seen in the carbonate globules in ALH84001 by inorganic means. I have shown that sid-magn solid solutions do decarbonate to form nanometer-sized magnetite crystals, with crystal shapes very much like those described from ALH84001 [1, 2, 5].

This study does not discount the "life on Mars" theory, but it does show a reasonable inorganic process can form magnetite grains that are similar to those formed by magnetotactic bacteria, and similar to those seen in ALH84001, as argued by [4] and [6]. If decarbonation occurred as hypothesized, it was under reducing, not oxidizing conditions, because no hematite or magnesioferrite is present in ALH84001.

References: [1] McKay, D.S., *et al.* (1996) *Science*, **273**, 924-930. [2] Thomas-Keptra, K.L., *et al.* (2000) *Geochim. Cosmochim. Acta*, **64**, 4049-4081. [3] Bradley, J.P., R.P. Harvey, and H.Y.J. McSween. (1996) *Geochim. Cosmochim. Acta*, **60**, 5149-5155. [4] Brearley, A.J. (1998) *LPSC XXIX*, Abstract # 1451. [5] Thomas-Keptra, K.L., *et al.* (2001) *Proc. of the Nat'l Acad.Sci. USA*, **98**, 2164-2169. [6] Golden, D., *et al.* (2001) *Amer. Mineral.*, **86**, 370-375 [7] Chai, L. and A. Navrotsky. (1994) *Amer. Mineral.*, **79**, p. 921-929. [8] Powell, H.E.(1965) *U.S. Bureau of Mines Report of Investigations*, **6643**,1-44. [9] Stubina, N.M. and J.M. Toguri (1989) *Trans. Iron & Steel Soc.*, **10**, 87-90.

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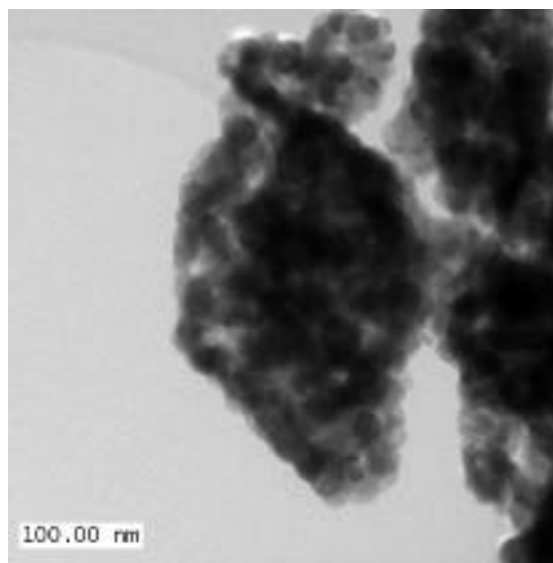


Figure 1: Bright field TEM image of a cluster of 10 – 20 nm magnetite grains, apparently forming a pseudomorph after a rhombohedral sid100 grain heated at reduced O₂ fugacity.

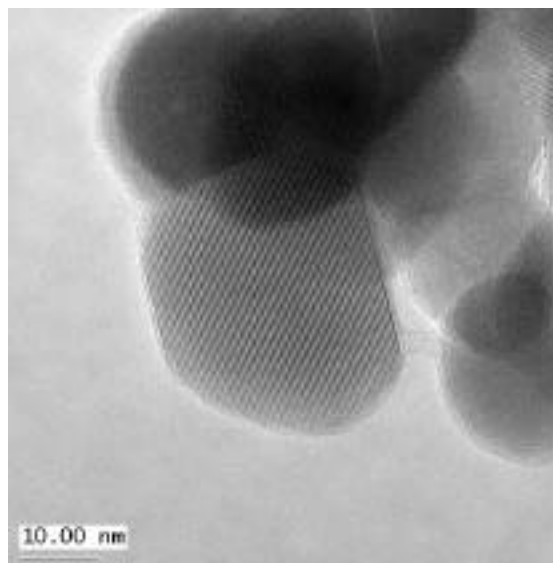


Figure 2: Bright field TEM image of a group of magnetite grains. Note lattice fringes of well-formed grain in center.