

## Nanophase magnetite and pyrrhotite in ALH84001 Martian meteorite: Evidence for an abiotic origin

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### Introduction:

The nanophase magnetite crystals in the black rims of pancake-shaped carbonate globules of the Martian meteorite ALH84001 have been studied extensively because of the claim by McKay et al. [1] that they are biogenic in origin. A subpopulation of these magnetite crystals are reported to conform to a unique elongated shape called “truncated hexa-octahedral” or “THO” [2]. They claim these THO magnetite crystals can only be produced by living bacteria thus forming a biomarker in the meteorite. In contrast, thermal decomposition of Fe-rich carbonate has been suggested as an alternate hypothesis for the elongated magnetite formation in ALH84001 carbonates (e.g., [3,4,5]). Here we provide the experimental and observational evidence for the inorganic formation of nanophase magnetite and pyrrhotite in ALH84001 by decomposition of Fe-rich carbonate in the presence of pyrite.

### Materials and Methods

Several siderite samples were used in this study, including synthetic siderite with Mg content from 0-9 mole % [6], natural siderite from Copper Lake, Antigonish County, Nova Scotia (34.5 mole % Mg), and natural siderite from Nova Scotia (11.4 mole % Mg). A natural pyrite of unknown origin was used as the sulfide source. Magnetite crystals were prepared by heating siderite crystals in a CO<sub>2</sub>/CO (95:5) gas stream at 450°C. Magnetite crystals were extracted from the remaining carbonate with acetic acid [6] and imaged under a JEOL 2000FX Transmission Electron Microscope (TEM). Magnetite morphology was observed by TEM images obtained by a tilt series passing through the {110}<sub>e</sub> zone axis where [111]•{110}<sub>e</sub> ≠ 0; which provides a 2-D projection that uniquely discriminates the [111]-THO from other elongated octahedral forms. To determine the mode of formation of iron sulfide in the presence of magnetite, Mg-siderite and pyrite (both components of ALH84001) were heated individually or together in open and closed systems at 550°C for 1 h, and at 350°C for 9 d for selected treatments. Resulting magnetite and sulfide assemblages were characterized by electron beam analytical procedures.

### Results and Discussion:

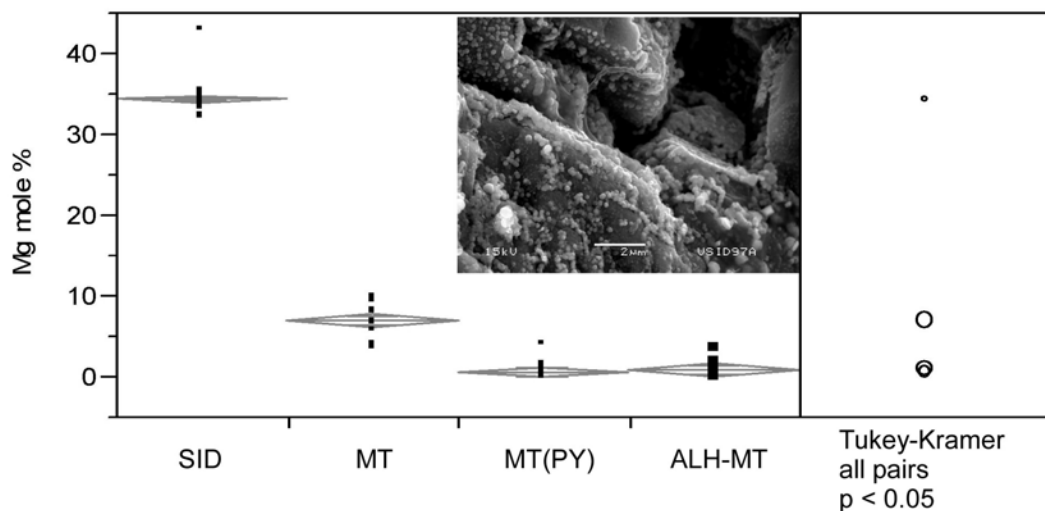
#### Magnetite Morphology:

The morphology of magnetite that formed by the thermal decomposition of pure synthetic siderite consisted of irregular, octahedral, and elongated octahedral forms. Elongated octahedral forms were classified as elongated simple octahedral ([111]-ESO), elongated cubo-octahedral ([111]-ECO) and truncated hexa-octahedral ([111]-THO). The [111]-ECO form was the most common, and a relatively few [111]-THO forms were also observed. A similar distribution was

found in magnetite crystals extracted from the ALH84001 carbonates in contrast to the earlier reports of a high abundance of THO elongated crystals [2]. We have earlier shown that the few crystals with THO morphology present in ALH84001 carbonates are a result of the natural variation in shapes of magnetite that form during the thermal decomposition of Fe-rich carbonate [6].

Pyrrhotite and magnetite formation:

Pyrrhotite has been identified as a sulfide mineral in ALH84001 carbonate globules; and along with magnetite they form the magnetic carriers in the meteorite [7]. Pyrite is the major sulfide mineral in the meteorite. Pyrrhotite may have formed by the thermal decomposition of pyrite and/or by the reaction of sulfur vapor from the thermal decomposition of pyrite reacting with Fe from siderite. This may take place in a closed system as the S vapor needs to be contained in order for siderite to convert to magnetite and pyrrhotite. The closed system heating of Mg-siderite and pyrite at low temperature over time produces all the important features previously attributed to biogenicity of magnetite in the Martian meteorite ALH84001; namely, the chemically pure, hexa-octahedral magnetite particles association with pyrrhotite. Hence, the products generated by the thermal decomposition of siderite and pyrite provide strong evidence for the inorganic formation of magnetite and pyrrhotite in Martian meteorite ALH84001 (Figure 1).



**Figure 1:** Magnesium composition of the original, natural Mg-siderite (SID) and magnetite (MT) products after heating at 350°C [when heated alone (MT) and with pyrite (MT(PY)) (see inset SEM for magnetite prior to extraction)]. Note the markedly decreased Mg content in magnetite compared to original carbonate. Mg content in magnetite from ALH84001 carbonates (ALH-MT) and those that from by the thermal decomposition of Mg-siderite in the presence of pyrite (MT(PY)) are indistinguishable (overlapping circles in the right hand side box indicate that there is no significant difference at  $p < 0.05$ ). Top and bottom edges of the diamonds represent the confidence intervals at  $p < 0.05$ .

**References:** [1] McKay et al. (1996) *Science*, 273,924-930. [2] Thomas-Keprta et al. (2001) *PNAS*, 98, 2164-2169. [3] Brearley (1998) *Lunar & Planetary Science XXXIX*, Abstract # 1451 CD-ROM. [4] Brearley (2003) *Meteoritics & Planetary Science*, 38, 849-870. [5] Treiman (2003) *Astrobiology*, 3,369-392. [6] Golden et al. (2004) *American Mineralogist*, 89, 681-695. [7] Weiss et al. (2002) *Earth & Planetary Science Letters*, 201, 449-463.