Origin of magnetite crystals in Martian meteorite ALH84001 carbonate disks

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Background and Introduction: Martian meteorite ALH84001 preserves evidence of interaction with aqueous fluids while on Mars in the form of microscopic carbonate disks which are believed to have precipitated ~3.9 Ga ago at beginning of the Noachian. Intimately associated within and throughout these carbonate disks are nanocrystalline magnetites (Fe$_3$O$_4$) with unusual chemical and physical properties, whose origins have become the source of considerable debate. One group of hypotheses argues that these Fe$_3$O$_4$ are the product of partial thermal decomposition of the host carbonate. Alternatively, the origins of Fe$_3$O$_4$ and carbonate may be unrelated; that is, from the perspective of the carbonate the magnetite is allochthonous. We have sought to resolve between these hypotheses through the detailed characterized of the compositional and structural relationships of the carbonate disks and associated magnetites with the orthopyroxene matrix in which they are embedded [1]. We focus this discussion on the composition of ALH84001 magnetites and then compare these observations with those from our thermal decomposition studies of sideritic carbonates under a range of plausible geological heating scenarios.

Methods: \(\text{ALH84001} \). Seven focused ion beam (FIB) sections were extracted from two carbonate disks -- three from the disk inner cores and four from the thin rims which surround the cores. Sections were analyzed by high resolution transmission electron microscopy (TEM) equipped with light element energy dispersive X-ray spectroscopy (EDX).

Roxbury Siderite. To investigate the chemical compositions of magnetite formed from the decomposition of Fe-rich carbonates, a sample of Roxbury siderite, having a bulk composition of \((\text{Fe}_{0.84}\text{Mg}_{0.10}\text{Mn}_{0.04}\text{Ca}_{0.02})\text{CO}_3\) [2], was decomposed using two different heating regimes -- ‘slow’, (~$10^4$ K/sec; identical to that used by [3]), and ‘fast’ (~$10^8$ K/sec) using a pulsed CO$_2$ laser to simulate the rapid heterogeneous heating. Unheated samples served as controls. Siderite samples invariably yields impure Fe-oxide.

Results: \(\text{ALH84001} \). Carbonate disks can be envisioned as being composed of three concentric annular zones; the center composed of an inner and outer core surrounded by a thin rim composed of optically alternating black-white layers. ALH84001 magnetites are embedded within all compositions of carbonate ranging from the most Fe-rich \((\text{Fe}_{0.60}\text{Mg}_{0.16}\text{Ca}_{0.03}\text{Mn}_{0.04})\text{CO}_3\) at the disk core to essentially Fe-free magnesite with the highest population of conditions (see references in [1]) and are in stark contrast to the pure magnetites in ALH84001 carbonate disks.

Discussion & Implications: Although thermal decomposition hypotheses for the observation of chemically pure magnetites in ALH84001 carbonate disks appears, on the surface, to provide a simple inorganic explanation of the observations, it is not applicable to the formation of the vast majority of ALH84001 magnetites. For example, it is difficult to suggest a process by which the magnesite, which is essentially Fe-free, decomposed to form magnetite. Furthermore, it would be difficult to explain the presence of chemically impure magnetites with minor to trace amounts of Cr since this element cannot substitute into the trigonal \((\text{Fe}_{3}\text{C})\) structure of carbonate.

Thermal decomposition of Roxbury siderite under both ‘fast’ and ‘slow’ heating resulted in the formation of impure (Mg,Ca,Mn)-ferrites. These findings agree with prior decomposition studies performed under a wide variety of conditions (see references in [1]) and are in stark contrast to the pure magnetites in ALH84001 carbonate disks.

The presence of chemically pure ALH84001 magnetite is inconsistent with formation by thermal decomposition of the host carbonate. We suggest that the majority of ALH84001 magnetites has an allochthonous origin and was added to the carbonate system from an outside source. This origin does not exclude the possibility that a fraction is consistent with formation by biogenic processes, as proposed in previous studies.