NEW INSIGHTS INTO THE ORIGIN OF MAGNETITE CRYSTALS IN ALH84001 CARBONATE DISKS

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Introduction: Martian meteorite ALH84001 preserves evidence of interaction with aqueous fluids while on Mars in the form of microscopic carbonate disks believed to have formed ~3.9 Ga ago at beginning of the Noachian epoch. Intimately associated within and throughout these carbonate disks are nanocrystal magnetites (Fe_3O_4) with unusual chemical and physical properties. The origin(s) of these magnetites has(have) become the source of considerable debate. One group of hypotheses argues that these magnetites are the product of partial thermal decomposition of the host carbonate; this decomposition event being separately argued to have occurred under the mutually exclusive conditions of kinetic or pseudo-equilibrium control. Alternatively, we have argued that the origins of magnetite and carbonate are unrelated; that is, from the perspective of the carbonate the magnetite is allochthonous. This hypothesis is based on two lines of research: (1) the comprehensive, detailed characterized of the compositional and structural relationships between the carbonate disks, their associated magnetites and the orthopyroxene matrix in which they are embedded [1]; and, (2) the results of experimental thermal decomposition studies of sideritic carbonates, conducted under a range of heating scenarios, which have repeatedly failed to produce magnetite nanocrystals with the chemical and physical properties of those present in the ALH84001 carbonate disks.

Methods: Seven focused ion beam (FIB) transverse sections were extracted from two carbonate disks -- three spanning the inner disk cores and four from the thin rims surround the cores. Extracted FIB sections were either *Pt*-welded *in situ* onto a *Cu* TEM crescent lift-out grid, or placed *ex situ* onto a continuous *C* film *Cu* TEM grid. Sections were analyzed by high-resolution transmission electron microscopy (HRTEM) equipped with light element energy dispersive X-ray spectroscopy (EDX).

To investigate the chemical and physical properties of magnetite formed through thermal decomposition, a sample of Roxbury siderite ($(Fe_{0.84}Mg_{0.10}Mn_{0.04}Ca_{0.02})CO_3$ [2]) was used as a standard. This was decomposed using two different heating regimes; 'slow' ($\frac{\partial T}{\partial t}$ ~ 10^{-2} K·sec^{-1}) and 'fast' ($\frac{\partial T}{\partial t}$ ~ 10^8-10^9 K·sec^{-1}) to produce magnetites formed under both kinetic and thermodynamic control. An unheated sample served as a control and all samples were embedded in epoxy and sectioned for analysis by diamond knife ultramicrotomy.

Results: *ALH84001*. Carbonate disks can be envisioned as being composed of three concentric annular zones. Moving out from the center there is an inner and outer central core which is itself surrounded by a thin rim composed of optically alternating black-white-black layers. ALH84001 magnetites are embedded within all compositions of carbonate, including the *Fe*-free magnesite ($MgCO_3$) present in the white layer of the outer rim (Fig. 1). The highest density of magnetites occurs within the two black layers of the outer rim. The majority of magnetites are stoichiometrically pure Fe_3O_4 although there were several notable exceptions, e.g., a small fraction of magnetites contain minor to trace amounts of *Cr*, which was undetectable in the surrounding host carbonate (Fig.2).

Roxbury Siderite Control Sample. The bulk composition of Roxbury siderite is analogous to the most *Fe*-rich component of the ALH84001 carbonate disks ($(Fe_{0.75}Mg_{0.24}Mn_{0.003}Ca_{0.004})CO_3$ [3]. However, TEM characterization at the sub-micron scale reveals significant variations in *Fe*:*Mg* ratio relative to the bulk composition and appeared to be correlated with grain size. The fine grain (<100 nm) component is *Mg*-poor (*Fe*:*Mg* > 20:1) while, the coarse grained component is relatively *Mg*-rich (*Fe*:*Mg* < 8:1). In both size ranges *Mn* and *Ca* are uniform in comparison.

Roxbury Siderite 'Fast' and 'Slow' Heated Samples. Under both 'fast' and 'slow' heating regimes, decomposition of Roxbury siderite resulted in the formation of impure ferrites with the with variable *Mg* and a relatively invariant *Mn* content. (Fig. 3). Since the *Mg* and *Mn* variation mirrors that of the unheated carbonate this variation is simply a reflection of the initial content of the carbonate. Notably, in neither the 'fast' or 'slow' products did we find any evidence for discrete *MgO* or *CaO* phases.

These results, in conjunction with prior carbonate decomposition studies of the *Fe*-, *Mg*- and *Ca*-ternary carbonates (*e.g.*, [4,5] and references in [1]), demonstrate that the decomposition of impure, cation substituted siderites invariably yields impure *Fe*-oxides.

Discussion & Implications: Thermal decomposition of Roxbury siderite under *both* 'fast' and 'slow' heating resulted in the formation of impure (*Mg*,*Ca*,*Mn*)-ferrites. These findings are in agreement with prior decomposition studies performed under a wide variety of conditions and the thermal decomposition of mixed cation siderite can be summarized as:

$$3(\mathrm{Fe}_x\mathrm{Mg}_y\mathrm{Ca}_z\mathrm{Mn}_{[1-x-y-z]})\mathrm{CO}_3 \xrightarrow{\Delta} (\mathrm{Fe}_x\mathrm{Mg}_y\mathrm{Ca}_z\mathrm{Mn}_{[1-x-y-z]})_3\mathrm{O}_4 + 2\mathrm{CO}_2 + \mathrm{CO}$$

While the thermal decomposition hypotheses for the origin of magnetites in ALH84001 carbonates is appealing in its simplicity it is nonetheless inapplicable since magnetites formed this way fail to show the chemical and physical properties characteristic of magnetites we actually do observe in ALH84001 carbonate disks. 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 ($R\bar{3}c$) structure of carbonate.

We argue that the majority of ALH84001 magnetites has an allochthonous origin, that is they were incorporated from an outside source in to the carbonate. This origin does not exclude the possibility of formation by biogenic processes, as has been proposed in previous studies.

References: [1] Thomas-Keprta *et al.* (2009) *GCA* **73**,6631-6677. [2] Lane, M. & Christensen, P. (1997) *JGR*, 102, 25581-25592. [3] Treiman, A.H. (2003) *Astrobiology*, 3, 369-392. [4] Jiménez López, C. *et al.* (2008) *AGU*, #P51A-1405. [5] Gotor, F.J. *et al.* (2000) *Phys. & Chem. of Min.*, 27, 495-503.

Fig.1. *Left*: TEM view of ALH84001 magnetites (arrows) embedded within the magnesite layer. *Right*: EDX spectra for one of the magnetites (red circle), the surrounding magnesite matrix (blue circle), and the difference spectrum (green). They show the host matrix is essentially *Fe*-free while the magnetite is *Mg*-free. The presence of these magnetites embedded in the magnesite band indicates they could not have formed by thermal decomposition of the magnesite matrix.

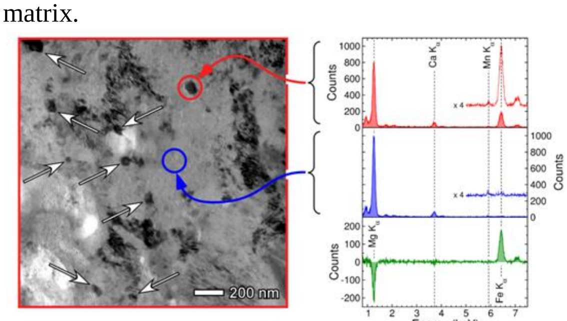

Fig.2. *Top views*: FIB section extracted from the core-rim interface of an ALH84001 carbonate disk (left) and high magnification of magnetite crystals within that section (right). *Bottom views*: Element maps for *Fe* (left) and *Cr* (right) of the largest magnetite in the field of view (top right). This magnetite has a composition of *Fe* ~70.1 wt.%, *Cr* ~ 2.3 wt.%, and *O* ~27.6 wt.%, corresponding to a stoichiometry of $(Fe_{2.9}Cr_{0.1})O_4$ (*i.e.*, ~ 3.3% Cr_2O_3).

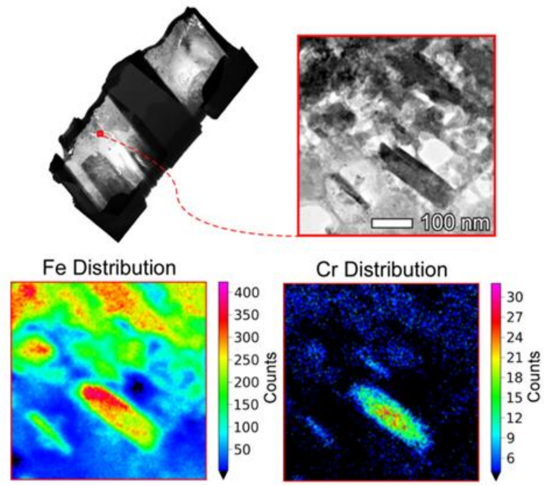

Fig. 3. EDX spectra and TEM views of magnetites formed from the 'slow' (green box) and 'fast' (blue box) heating of Roxbury siderite. Although spatially associated, variations in *Mg* content are apparent while *Mn* content is relatively uniform. All magnetites formed from the thermal decomposition of Roxbury siderite contained chemical impurities reflecting the composition of the precursor Roxbury siderite.