Origins of magnetite nanocrystals in Martian meteorite ALH84001

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Abstract

The Martian meteorite ALH84001 preserves evidence of interaction with aqueous fluids while on Mars in the form of microscopic carbonate disks. These carbonate disks are believed to have precipitated 3.9 Ga ago at beginning of the Noachian epoch on Mars during which both the oldest extant Martian surfaces were formed, and perhaps the earliest global oceans. Intimately associated within and throughout these carbonate disks are nanocrystal magnetites (Fe3O4) with unusual chemical and physical properties, whose origins 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. Alternatively, the origins of magnetite and carbonate may be unrelated; that is, from the perspective of the carbonate the magnetite is allochthonous. For example, the magnetites might have already been present in the aqueous fluids from which the carbonates were believed to have been deposited. We have sought to resolve between these hypotheses through the detailed characterization of the compositional and structural relationships of the carbonate disks and associated magnetites with the orthopyroxene matrix in which they are embedded. Extensive use of focused ion beam milling techniques has been utilized for sample preparation. We then compared our observations with those from experimental thermal decomposition studies of sideritic carbonates under a range of plausible geological heating scenarios. We conclude that the vast majority of the nanocrystal magnetites present in the carbonate disks could not have formed by any of the currently proposed thermal decomposition scenarios. Instead, we find there is considerable evidence in support of an alternative allochthonous origin for the magnetite unrelated to any shock or thermal processing of the carbonates.

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1. INTRODUCTION

The Allan Hills 84001 (ALH84001) meteorite is a coarse grained orthopyroxenite that solidified from a melt ~4.51 Ga ago (Nyquist et al., 2001). Approximately 600 Ma later (Borg et al., 1999), secondary carbonates were deposited by low temperature hydrothermal processes in pre-existing fractures and fissures within the groundmass.
Chemically the disk carbonates have a complex mixed cation composition with an empirical formula \((\text{Fe}^x\text{Mg}^y\text{Ca}^z\text{Mn}^{1/2}\text{Co}^x\text{Co}^y\text{Co}^z)\text{CO}_3\) where \(x + y + z = 1\). The values of \(x\), \(y\), and \(z\) vary with radial distance in such a way that the carbonate disks can be envisioned as being composed of three concentric annular zones; starting from the center there is an inner central and outer core surrounded by a thin rim. Embedded within these carbonates are discrete nanocrystal magnetites \((\text{Fe}_x\text{O}_y)\) that exhibit super-paramagnetic to single-domain properties (Muxworthy and Williams, 2008). While the largest population of these magnetites occurs within the rim zone of the carbonate disks, e.g., McKay et al. (1996) and Thomas-Keprta et al. (2000a), a small but significant fraction is also found within the inner and outer core zones.

When the carbonate disks were initially characterized, they were interpreted as products of high temperature processes \((T > 573\,\text{K})\) (Harvey and McSween, 1996; Mittlefehldt, 1994a; Mittlefehldt, 1994b; Scott et al., 1997). Subsequently, isotopic and chemical data has forced a revision in this interpretation and it is now generally accepted they were deposited by low temperature \((T < 573\,\text{K})\) hydrothermal processes (Eiler et al., 2002; Kent et al., 2001; Kirschwink et al., 1997; McSween and Harvey, 1998; Romanek et al., 1994; Saxton et al., 1998; Treiman, 1997; Valley et al., 1997; Warren, 1998). While the consensus of opinion on the temperature of formation of the carbonates has converged, that of their subsequent thermal evolution has not because of the differing hypotheses invoked to explain the presence of the nanocrystal magnetites present within the carbonate. To first order, these magnetites were either already present when the carbonates formed and so became embedded during carbonate deposition, or they were formed \(a\ posteriori\) by partial thermal decomposition of the pre-existing carbonate. In the latter case, the heating of the meteorite is envisioned to have occurred through the adiabatic propagation of one or more impact shock events.

Fig. 1A. Optical images of ALH84001 disk-like carbonates. These disks precipitated in fractures produced during shock impacts while the meteorite was on Mars. The majority of these carbonates appear as circular or elliptical features which range from ~10 to 300 \(\mu\text{m}\) along the major axis. Visually they have colors that vary from gold to burnt orange in their centers which are typically surrounded by a thin black–white–black rim. Some carbonates occur as single entities while others are spatially associated and occur in groups of 10s of carbonates (image at far right). The black rims typically range from ~5–10 \(\mu\text{m}\) in thickness and are composed primarily of nanophase magnetite embedded in a matrix of Mg-bearing sideritic carbonate while the white bands, typically ~10–15 \(\mu\text{m}\) thick, are composed of nearly pure magnesite with minor Ca and nanophase magnetite.

Fig. 1B. Illustration of an inverted conic frustum, that is, the polygon which remains after a cone is cut by a plane parallel to the base with the apical part removed and the remaining polygon inverted. While single ALH84001 carbonates have been loosely described as rosettes, globules, concretions, or pancakes, they are more accurately described as being shaped like an inverted conical frustum.
ALH84001 shows evidence of having undergone multiple impact events, the last resulting in its ejection from Mars, e.g., Treiman (1998). In general, the peak shock pressures experienced by Martian meteorites are thought to range from less than 14 gigapascals (GPa) up to ~55 GPa (Fritz et al., 2004; Fritz et al., 2003; Langenhorst et al., 2000; Stöffler, 2000; Treiman, 2003; van der Bogert et al., 1999). These estimates are based on the conversion of plagioclase to either a diaplectic ‘maskelynite’ (~14–45 GPa) or melt glass (~>45 GPa) with a resulting increase in the refractive index and/or Raman band broadening, compared to unshocked plagioclase (Fritz et al., 2004). Specifically, for ALH4001, estimated values for peak shock pressure have evolved over time – ~50–60 GPa (Langenhorst et al., 2000); <40 GPa (van der Bogert et al., 1999); ~35–40 GPa (Stöffler, 2000); 35.7 ± 4.5 GPa (Fritz et al., 2003); >35–40 GPa (Fritz et al., 2004) – with the best current estimate at 32 ± 1 GPa (Fritz et al., 2005).

The extent to which impact shocks to ALH84001 lead to thermal excursions that could have partially decomposed the ALH84001 carbonate disks remains ambiguous (note, in this context any impacts occurring in the ~600 Ma prior to carbonate formation have no bearing). Results from simulations of shockwave propagation through compositionally and texturally complex matrices are computationally difficult and sensitive to initial starting conditions, but do indicate that shock heating would have been highly heterogeneous at all size scales. Using a Hugoniot equation-of-state experimentally derived from Stillwater pyroxenite, Twin Sister dunite (Stöffler, 1982), and a gabbric rock (Trunin et al., 2001), the post-shock temperature elevation for ALH84001 associated with a 32 GPa shock event lies in the range of ~373–383 K (Fritz et al., 2005). If we assume ALH4001 prior to ejection was at the average Martian ground-surface temperature of ~230 K and that the peak shock pressure experienced corresponded to this final ejection event (note, paleomagnetic data of Weiss et al. (2000) suggest the interior of ALH84001 was not heated above ~313 K), this would imply an average maximum heating, post-ejection, to a temperature of ~610 K. This is in broad agreement with recent (U–Th)/He analyses of ALH84001 phosphate grains that suggest a peak ejection temperature of ~673 K or less (Min and Reiners, 2006).

To address these unresolved questions we have utilized focused ion beamsing techniques in conjunction with conventional ultramicrotomy to provide the most detailed picture yet of the spatial, structural and chemical relationships present within ALH84001 carbonate disks. We have then used these new observations to evaluate the merits of both theoretical and experimental attempts to reproduce ALH84001-like disks with embedded magnetites through partial thermal decomposition of Fe-bearing carbonate. In the larger context, resolving or at least constraining the origin of the magnetites within ALH84001 carbonate disks has importance in that it has been previously suggested that the precipitation of the carbonate disks may have been facilitated through biogenic activity (McKay et al., 1996) and that a fraction of the embedded magnetites exhibit chemical and physical features identical to those produced by contemporary magnetotactic bacteria (McKay et al., 1996; Thomas-Keprta et al., 2000a; Thomas-Keprta et al., 2001; Thomas-Keprta et al., 2002).

2. METHODOLOGY

2.1. ALH84001 carbonate disks

Table 1 lists the ALH84001 rock splits used in the research presented herein. Prior to any extraction, fracture surfaces containing carbonate disks were first characterized by optical and electron microscopy. This involved optical imaging under both bright and dark-field illumination conditions. Given the topographic variations present within a given fracture surface, a long working distance Nikon Eclipse ME600 microscope was used for this task. Due to the low numerical apertures associated with long working distance microscope objectives, the depth-of-field was

<table>
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Table 1
Rock splits of Martian meteorite ALH84001.
mechanical stress, so that the size of the thin section that can be obtained is limited only by the tendency of large area surfaces to eventually warp or curl due to differences in surface tension between and across adjacent faces. In practical terms for ~150 nm thick carbonate thin sections we found the length-to-thickness (l/w) ratio could not practically exceed ~200, with the largest FIB section extracted here being ~20 μm in length (l/w ~ 130).

In all, seven FIB thin sections were acquired using the standard ‘H’-bar extraction procedure from two carbonates on unrelated fracture surfaces as documented in Table 2. Sections were prepared using either a FEI Dual-Beam Strata 237 (‘Texas’ Sections 1 and 2; ‘Posterboy’ Sections 1–4) or Strata 400 (‘Posterboy’ Section 5) workstations. Both instruments were equipped with a field emission electron source, a Ga⁺ ion source, a 30 kV scanning TEM detector, an EDX spectrometer, and an Omniprobe in vacuo micro-manipulator. Sample mounting used the same 1/2-inch Al pin mounts used in the preliminary SEM imaging. The first two FIB thin sections were acquired from an interior carbonate fragment designated ‘Texas’ plucked from a freshly exposed OPX fracture surface of rock split ALH84001,286. Both sections were transferred directly to a continuous C film Cu TEM grid. The remaining five FIB thin sections were extracted from both core and rim of a carbonate disk designated ‘Posterboy’ located on a freshly exposed fracture surface of rock split ALH84001,386. Note that for these sections the carbonate was not removed from its fracture surface, rather the entire chip containing the fracture surface was mounted in the FIB instrument. This was done in order to permit the study of both carbonate and the interface with the surrounding and underlying OPX. Each removed thin section was welded on one or both sides in situ to a Cu crescent TEM mount.

Both ultramicrotome and FIB thin sections were analyzed using either a JEOL 2000 FX 200 kV STEM and/or a JEOL 2500SE 200 kV field emission STEM. Both instruments were equipped with light element (Z > 5) Si-drift EDX detectors (Noran System 6), and in the case of the 2500SE, a modified objective-lens pole piece allowed a colimator-equipped 0.3 steradian large area (50-mm²) EDX detector for increased sensitivity. The JEOL 2500SE instrument was also equipped with a Gatan Tridimen Imaging Filter for energy-filtered imaging and electron energy-loss spectroscopy, and a high-angle annular darkfield detector for z-contrast imaging.

2.2. Roxbury siderite

To investigate the chemical compositions of magnetite formed from the decomposition of Fe-rich carbonates, a
186 g sample of siderite (FeCO₃) from the Roxbury iron mine in Litchfield, Connecticut was obtained from the Excalibur Mineral Company. Roxbury siderite has previously been reported as having a bulk composition of (Fe₀.₆₄Mg₀.₃₆)₂O(CO₃)₀.₀₄ (Lane and Christensen, 1997) and provides (compositionally) a reasonable terrestrial analog to the Fe-rich component of ALH84001 carbonates. It is a composition of (Fe₀.₇₅Mg₀.₂₄Mn₀.₀₀₃Ca₀.₀₀₄)CO₃ which was calculated by Treiman (2003) for the inner rim of a carbonate disk.

Three separate sample fractions of Roxbury siderite were prepared by mechanical abrasion from the bulk sample. One fraction served as a control while the remaining two were thermally decomposed. In one case, decomposition occurred under a very slow, controlled heating rate, while in the other, the heating event was essentially instantaneous. We will, for brevity, subsequently refer to these heating scenarios as either being ‘slow’ or ‘fast’, respectively.

In the ‘slow’ heating experiment the large sealed quartz tube (LSQT) method was used to produce a closed reaction under conditions approximating thermal equilibrium (Lauret et al., 2005). In this method, the siderite sample is placed in small open quartz crucible, which is in itself within a larger evacuated quartz tube, along with a second crucible containing lime (CaO). The whole assembly is heated in a vertical tube furnace, with the temperature being controlled using a J-type thermocouple attached to the LSQT. In our experiment, the siderite sample was heated at a rate of 1 K·min⁻¹ to a maximum temperature of 848 K, after being held at this temperature for 24 h, it was cooled back to room temperature at a rate of ~ −10⁻² K·s⁻¹.

In the ‘fast’ heating experiment, the siderite sample was heated under vacuum with a pulsed 10.6 μm CO₂ laser (PRF-150 Laser Science, Inc.) focused onto the sample using a Cassegrainian microscope objective. The temporal profile of the CO₂ laser pulse had a ~300 ns initial spike accounting for ~30% of the total pulse energy which was then followed by a slow oscillatory decay extending up to ~1–2 μs. Results using a thin-film Pt thermocouple suggest that the heating rates were on the order of ~10⁸–10⁹ K·s⁻¹ with a peak temperature of ~573–673 K being reached at the laser focus (Zenobi et al., 1995).

3. RESULTS

3.1. ALH84001 carbonate disks

3.1.1. Spatial location and distribution of carbonate disks

Carbonates account for ~1% by volume of ALH84001 and are distributed throughout the multiple internal fracture surfaces that pervade the meteorite (Mittlefehldt, 1984a; Mittlefehldt, 1984b). While single isolated carbonates do occur, most often they are found in clusters ranging from a few to tens of carbonates, some of which appear partially fused (Fig. 1A). These carbonates are not simple vein-filling deposits since their center-of-mass lies not between the adjacent fracture surfaces, but rather, is offset such that the carbonate disk is either mostly or wholly inset within a form-fitting pit in one or other surface. Intriguingly, in fractures in which multiple carbonates are present, the pits in which each of the carbonates are inset all lie on the same OPX surface. A priori it might be expected that the carbonate pits would be evenly distributed between the adjacent fracture surfaces, however, this is not so.

3.1.2. External shape of ALH84001 carbonate disks

The carbonate disks within each OPX pit show a relatively constant thickness that does not change, proceeding from the core outward, until the onset of the inner magnetite band where upon it abruptly decreases, in an approximately linear fashion, all the way to the carbonate edge. Hence, as noted previously, the most accurate terminology describing this shape is that of an inverted conic frustum, see Fig. 1B, as opposed to the more widely used, but inaccurate description, as disks, rosettes, or pancakes. In general, while the diameter of carbonate disks can vary by a factor of 10 or more, even within a single fracture surface, the thickness is relatively invariant being typically ~10–15 μm. Consequently this implies that the radial thickness of the carbonate rims must also be similarly invariant, as is observed with a typical width of ~10 μm.

Fig. 1C. Backscatter electron image (BSE) of a partial, false-colored ALH84001 carbonate disk embedded within the OPX matrix of a freshly fractured chip. The uppermost surface of the carbonate lies flush with the surrounding OPX (gray). The body of the carbonate disk is inset within a form-fitting depression ~5 to 8 μm deep within the OPX. All ALH84001 carbonate disks we have investigated have this common morphological context.

1 In the rim region the inner and outer magnetite bands do not lie perpendicular to the fracture surface but rather are canted outward with acute angles φ and θ, where φ > θ and θ ~ (90 – φ), with φ being the angle between the generatrix and the axis of the conic frustum.
Carbonates are inset within form fitting pits and lie flush with the OPX fracture surface as illustrated in Fig. 1C. The OPX fracture surfaces in which carbonates are found all demonstrate an aligned striated texture, Fig. 1D and 1E, which can be interpreted as the result of differential weathering of OPX lamellae that is characteristic of partial aqueous chemical dissolution (Velbel, 2007). This texture contrasts sharply with that of the OPX underlying the carbonate which forms the base of the pits, which has a loosely oriented botryoidal or micro-denticular texture (Fig. 1F and 1G). These Martian ‘microdenticles’ share some physical similarities to terrestrial denticles formed by the low temperature aqueous alteration/weathering of chain-silicates (e.g., pyroxene, amphibole) (Velbel, 2007; Velbel et al., 2007). Although the majority of terrestrial denticles are larger in size than their putative Martian counterparts (up to 10s of microns in length) the lower end of the size distribution does overlap that of the Martian microdenticles (Velbel, 2007; Velbel et al., 2007). Hence, this suggests that the OPX textures, including pits and etched surfaces, formed either prior to, or contemporaneously, with the deposition of carbonate through a process of chemical dissolution of the silicate.

In the terrestrial context, aqueous weathering of chain-silicates results in the concurrent formation of other low temperature secondary minerals such as kaolinite (Si₂Al₂O₅(OH)₄), smectite³ and serpentinite⁴ clay minerals, and oxyhydroxides such as goethite (α-FeOOH) (Velbel, 2007). While there have been sporadic observations of smectites in ALH84001 (Thomas-Keprta et al., 2000b), generally the most remarkable observation is how scarce they appear to be. Given the age and uncertainty in the history of ALH84001, it is possible that such minerals might have once been present but were not preserved (Velbel, 2007), nevertheless the lack of such weathering minerals associated with ALH84001 fracture surfaces and their associated carbonate disks has yet to be satisfactorily explained and remains an enigma.

### 3.1.4. Surface textures of carbonate disks

SEM images of the upper surfaces of carbonate disks exposed to fracture space are shown in Fig. 1H and 1I. At low magnification, carbonates display a pitted texture interspersed with lamellar striations, while at high magnification the surface texture is composed of discrete particles ranging from ~20 to 250 nm with ovoid to irregular shapes. This texture is unlikely to represent the primordial texture of the carbonate at the time of its deposition, but rather represents the products of subsequent superficial erosion and carbonate dissolution during post-depositional fluid interactions.

### 3.1.5. Composition of ALH84001 carbonate disks

The largest carbonate within a cluster of carbonates on a freshly exposed fracture surface of ALH84001.286 was designated as the ‘Ear’ carbonate (Figs. 2A and 2B). This ‘Ear’ carbonate provides a good example of the typical carbonate

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² Pyroxenes have the general formula XY(Si,Al)₂O₆ (where X generally represents Na, Mg, Ca, and Fe²⁺ and Y generally represents Mg, Al, Sc, Ti, V, Cr, Mn, and Fe³⁺). Amphiboles have chemical compositions and general characteristics that are similar to the pyroxenes although extensive substitution of Si by Al can occur. The chief difference between amphiboles and pyroxenes is that the basic structure of an amphibole is a double chain of SiO₄ tetrahedra compared to a single chain structure for pyroxene.

³ The smectite group of minerals includes dioctahedral phyllosilicates including Fe³⁺-rich nontronite (Na₀.₃Fe₂(Si,Al)₄(OH)₂·nH₂O), Fe³⁺-poor montmorillonite ((Na,Ca)₀.₃₃(Al,Mg)₂-Si₄O₁₀(OH)₂·nH₂O) and trioctahedral clays including saponite with the general chemical formula Ca₀.₂₅(Mg,Fe²⁺)₃-(Si,Al)₂O₄(OH)₂·4H₂O.

⁴ Serpentinite represents a group of hydrous Mg, Fe-phyllosilicate ((Mg,Fe)₂Si₂O₅(OH)₃) minerals.
While there are compositional variations between carbonate disks, both on the same and different fracture surfaces, many of the broader characteristics demonstrated by the ‘Ear’ carbonate are representative of all carbonates, albeit to differing degrees. Hence we have used the ‘Ear’ carbonate as the archetype to describe the spatial and compositional relationships exhibited by carbonate disks. Fig. 2A shows quantitative 2-D cation distributions obtained by electron microprobe analyses of the ‘Ear’ carbonate, while Table 3 lists the bulk composition.

While at the one micrometer resolution limit of the electron microprobe the variations of Ca, Mg, Fe, and Mn cations appear complex and sometimes chaotic, at a broader scale clear radial symmetric zoning patterns are apparent that can be described as three approximately equivolume concentric zones: an inner core (~50 μm radius along the major axis; ~30 vol.%), surrounded by an outer core.

Fig. 1H and 1I. SEM view (H) showing the characteristic deeply ridged and pitted (e.g., honeycomb) textures of the carbonate disk contiguous with the OPX fracture surface. At higher magnification (I) this surface texture is comprised of a matrix of spheroidal, ovoid, and irregular-shaped grains ranging from ~10 to 300 nm along the longest axis. Note that this surface texture is independent of the underlying carbonate composition, that is, the magnetite-rich rims display a texture nearly identical to that of the core carbonate.
The simplest of the three zones is the rim which is composed of a relatively thick band of almost pure magnesite \((\text{MgCO}_3)\) (>90 mol.% Mg) which is bordered on its inner

\(~20 \mu\text{m thick radial band; } \sim30 \text{ vol.\%}, \) which itself is surrounded by a rim \(~20 \mu\text{m thick radial band; } \sim40 \text{ vol.\%} as illustrated in \textbf{Fig. 2B}.

Fig. 2A. BSE view of a single ALH84001 carbonate disk, designated as ‘Ear’ carbonate and its associated quantitative element distribution maps for Ca, Fe, Mn, Mg, and S, acquired by wavelength dispersive electron microprobe analyses using a \(~1 \mu\text{m} \) probe beam. The region we designate as the inner core is characterized a significant enrichment in Ca and Mn, with both showing oscillatory, radial zoning patterns. The region that separates the inner core from the rim we designate as the outer core. The transition between the inner and outer core is characterized by a sharp \((<1 \mu\text{m}) \) compositional boundary in Ca and Mn distribution. The major cation distribution (Ca, Mg, Fe, and Mn) in this outer core is radially invariant, that is it changes little with increasing radius. Enrichment of S in the inner and outer magnetite-rich rims is attributed to the presence of nanophase Fe-sulfides.
and outer perimeter by thin Fe-rich bands composed primarily of magnetite embedded in a Mg:Fe (~60:40) carbonate matrix. Within the rim lies the outer and inner cores of which the latter is the compositionally most complex. At its very center, the inner core has a Ca-rich (Ca:Mg:Fe:Mn ~ 45:30:15:10) nucleus (75 × 20 μm major/minor axis) accounting for ~5% of the total volume of the carbonate. This is encircled by a thin (~10 μm) Ca-rich halo (Ca:Mg:Fe:Mn ~ 30:30:30:10) separated from the nucleus by a thin band (~10 μm) of Mg–Fe-rich carbonate (Mg:Fe:Ca:Mn ~ 40:40:16:4). Beyond the Ca-rich halo, the Ca concentration decreases proportionally to increasing Mg, while Fe concentration remains relatively invariant. Although Mn is always the minor cation, its relative abundance closely correlates with that of the Ca cation distribution, and is loosely inversely correlated to the Fe cation distribution. The outer core which separates the inner core from the rim is characterized by Ca, Mg, Fe, and Mn cation distributions that do not change significantly with changing radius, i.e., they are radially invariant.

Another way to visualize the compositional differences between the inner and outer cores and rim is to use the Ca, Mg, Fe + Mn ternary diagram in which the carbonate compositions associated with these three zones can then be seen to form three separate, but partially overlapping, density ellipses (Fig. 2C). For comparison to Fig. 2C, the Ca, Mg, Fe ternary diagram outlining the stability fields for calcite (CaCO₃), dolomite (Mg₃Ca(CO₃)₂) – ankerite (Ca,Fe(CO₃)₂), and the complete magnesite-siderite solid solution series is shown in Fig. 2D. It is apparent that the compositions of many ALH84001 core and rim carbonates lie outside of these thermodynamic stability fields. Combined with the complex radial oscillatory zoning and sharp compositional boundaries observed, it is clear that ALH84001 carbonate disks represent assemblages in a high degree of disequilibrium, consistent with the chemical and isotopic findings from previous studies, e.g., Treiman (1997) and Valley et al. (1997). If the carbonate disks evolved by successive radial deposition of carbonate from a central nucleus it would therefore imply that the pore- or fracture-filling fluid was out of thermodynamic equilibrium with the surrounding rock matrix, and that variations in diffusion parameters led to the development of the complex deposition patterns. This is commonly observed in environments where the rate of fluid-rock mass transfer is limited by diffusion. The observed complex mineral zonation patterns thus record the changes in the fluid composition caused by variable kinetic dispersion and fluid flow rates at the site of crystal growth. Oscillatory patterns formed where the rate of

Table 3
Electron microprobe analyses of ALH84001 ‘Ear’ carbonate.

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<th>Min. (mol.%)</th>
<th>Max. (mol.%)</th>
<th>Ave. 1 (mol.%)</th>
<th>Weighted Ave. 241 analyses (mol.%)</th>
<th>ALH84001 Carbonate Ave. (mol.%) (Mittlefehldt, 1994b)</th>
<th>Roxbury Siderite Ave. (mol.%) (Lane and Christensen, 1997)</th>
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<td>0.526</td>
<td>0.172 ± 0.115</td>
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<tr>
<td>Mn</td>
<td>0.001</td>
<td>0.098</td>
<td>0.030 ± 0.024</td>
<td>0.018</td>
<td>0.011</td>
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diffusion was sluggish enough to permit the establishment of sharp stationary chemical potential gradients.

3.2. ALH84001 FIB sections

SEM images of ‘Texas’ and ‘Posterboy’ carbonates prior to and after FIB extraction are shown in Figs. 3A and 3B, respectively. TEM overview images of ‘Texas’ FIB Sections 1 and 2, and ‘Posterboy’ FIB Sections 1–5 are shown in Figs. 3C–3I, respectively. Rather than discuss each section individually, for succinctness Fig. 4 summarizes the underlying characteristics of the rim and core carbonate structures observed in these sections.

3.2.1. Sections of rim carbonate: ‘Posterboy’ Sections 1–5

Compositionally the inner and outer magnetite rims are composed of an approximately 50:50 vol.% mixture of fine grained carbonate and single crystal magnetites (Figs. 2A and 2B; Fig. 5A), with Fe-sulfides also present as a minor phase (Fig. 5A). The carbonate has a Mg:Fe cation ratio of approximately 40:60 with minor and trace amounts of Mn and Ca, respectively. Pervading this carbonate is a poorly constrained, minor amorphous silica phase (Fig. 5A). Although this silica phase is also present throughout the entire carbonate, it is enriched ~3-fold within these rims. In some cases, we have also observed it to constitute a major phase and note that Si-rich veins in ALH84001 carbonates were also described by McKay et al. (1998). The magnetites are predominately stoichiometrically pure Fe3O4 (Fig. 5B), although some do contain Cr and/or Al (Fig. 5C) as noted previously by Thomas-Keprta et al. 2009.

Fig. 2C. Ternary cation plots for ‘Ea’ carbonate based on 449 electron microprobe spot analyses. In each plot the three cation end-members are Ca, Mg, and (Fe + Mn) and each data point is colored according to the mole fraction of Mn. In the top plot all 449 data points are show together while in the lower plots, data points corresponding to the inner and outer core and rims are shown plotted separately. The carbonate compositions associated with these three zones can be seen to form three separate, but partially overlapping, density ellipses. In the rim zone, the major axes of the density ellipse lies perpendicular to the Ca-end member calcite (CaCO3), encompassing a range of Ca-poor carbonate compositions with varying Fe: Mg ratios. Transitioning to the outer core, the density ellipse that encompasses these carbonates has a composition that, while overlapping the rim density ellipse, nevertheless has a slightly positive gradient with respect to the horizontal axis defined by the Mg- and Fe(Mn)-end member carbonates, magnesite and siderite (rhodochrosite; MnCO3). Hence, the more Fe-rich carbonates tend to be proportionally more Ca-rich, although the total fraction of Ca still remains low. The carbonate composition of the inner core shows a density ellipse that is almost perpendicular to that of both the outer core and rim, defining a range of Ca-rich to Ca-poor carbonates that share similar Mg:Fe ratios. The lower, Ca-poor, end of the density ellipse overlaps with that of the outer core while the upper Ca-rich end extends up to carbonates with an ankeritic (Ca,Fe(CO3)2)/dolomitic (Mg,Ca(CO3)2) composition. The different compositions of the inner and outer cores and rim are reflected in the separate data point clusters associated with each region. In the Ca-poor carbonate of the rim, the (Fe + Mn):Mg ratios are seen to vary nearly over the complete range between end-members. In the outer core, a smaller spread in (Fe + Mn):Mg ratios are observed and the carbonate tends to be proportionally more Ca-rich, although the total fraction of Ca still remains low. Finally in the Ca-rich inner core, the (Fe + Mn):Mg ratios are almost invariant relative to the mole fraction of Ca, which ranges up to almost an ankeritic-dolomitic composition. This results in an elliptical distribution of points with the major axis perpendicular to that defined by the (Fe + Mn) – Mg end members.
et al. (2000a). Sandwiched between the inner and outer magnetite bands is the almost pure magnesite band containing minor Ca and Si (Fig. 3G) and sporadic magnetite crystals (Fig. 3G).

Fig. 2D. Calculated thermodynamic stability phase diagram for Fe–Mg–Ca carbonates at 750 K and 1 bar pressure, using the approach of McSwiggen (1993a) and McSwiggen (1993b). Not all carbonate compositions are thermodynamically stable resulting in three distinct stability fields, highlighted in blue, corresponding to calcite, dolomite-ankerite, and the magnesite–siderite solid solution series. While the compositional range of ALH84001 carbonate disks extends into both the magnesite–siderite (2C; rim carbonate) and ankerite–dolomite stability fields (2C; inner core carbonate), most carbonate compositions lie between these stability fields indicating that for any given carbonate disk, taken as a whole, is in a state of thermodynamic disequilibrium. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Fig. 3A. BSE view of a partial ALH84001 carbonate disk designated 'Texas' that was removed from the OPX fracture surface in which it was embedded and transferred to electron conductive double-sided C tape (black background). The surface shown corresponds to the exposed surface which was contiguous with the OPX. Locations of the two core carbonate FIB sections that were extracted are shown by the boxes.

Fig. 3B. Optical (upper) and BSE (lower) views of ALH84001 carbonate disk designated 'PosterBoy.' In the upper optical image the carbonate is shown prior to FIB extraction (red boxes) while the lower BSE image was acquired after five separate FIB extractions, four of the rim and one of the core. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Morphologically the inner and outer cores and magnesite band are cross-cut by numerous veins (Figs. 3E, 3H and 3I, Figs. 5A and 5D) and open fractures (Fig. 3I), respectively, which must have formed after initial carbonate deposition. In the case of the magnesite band (Fig. 3I) most fractures appear open and are oriented along grain boundaries. A small percentage appears to be partially filled with an amorphous Fe phase(s) (Fig. 3I) that we have not yet been able to characterize. In the case of the outer core carbonate, there is extensive penetration by veins that radiate inward toward the inner core, either horizontally from the inner magnetite rim, or vertically from the upper carbonate surface (Figs. 3E, 3H and 3I, Figs. 5A and 5D). These veins are completely filled with a fine grained carbonate compositionally similar to the carbonate into which it intrudes. However, unlike the surrounding carbonate, the vein filling is intimately mixed with one or more amorphous silica phases (Figs. 5A and 5D) enriched by a factor of ~3 with respect to the surrounding carbonate, and contains embedded stoichometrically pure single crystal magnetites.
(Fig. 5B). These magnetites range in size from ~10 to 150 nm, and are similar to those observed in the inner and outer magnetite rims (Figs. 5A and 5C). Although magnetite-rich veins that cross-cut the outer cores are text-}

urally identical to those of the magnetite-rich rims, one difference between them is that the veins contain few or no detectable Fe-sulfides (Figs. 5A and 5D) arguing for a different mode of formation or a different generation.
3.2.2. ‘Posterboy’ Section 2 and ‘Texas’ Sections 1 and 2

The carbonate cores are predominantly composed of blocky interlocking, irregularly shaped carbonate crystals (Figs. 3C and 3D, 3F) ranging up to \( \approx 5 \mu m \) in size. Inter-spersed both within these crystals, and along grain boundaries (Fig. 3C), are sub-micron ‘void’ spaces which demonstrate a range of morphologies from amoeboidal to well faceted polygonal negative crystals (Fig. 3D). Only

Fig. 3C. Center: TEM image of ‘Texas’ FIB Section 1 extracted from the disk core (see 3A). The micron thick upper band of Pt was deposited as protection from Ga\(^{+}\) ion beam damage during FIB milling. The core region is composed of interlocking, mixed-cation, carbonate crystals ranging up to \( \approx 5 \mu m \) in size cross-cut by multiple veins. This coarse-grained interior texture contrasts sharply with that of the fine-grained upper surface texture described earlier (see Fig. 1I). Two regions of interest (ROIs) are indicated by red and blue boxes. Top views: Expanded view of ROI outlined by red box showing several veins cross-cutting the host carbonate. Veins are composed of fine grained (<100 nm) randomly oriented carbonate grains intimately mixed with an amorphous S-bearing phase that appears homogeneously distributed. The associated EDX spectrum was acquired using \( \approx 100 \) nm spot size and 1000 s dwell time. We suggest the veins formed by dissolution of core carbonate during exposure to a S-containing (possibly acidic) fluid. Lower views: expanded view of ROI outlined by blue box showing numerous nanophas_e magnetite and voids which appear to comprise <1 vol.\% of the total FIB section in this TEM view. During full TEM rotation (±44°) a significant increase of magnetite crystals (up to ~5 vol.\%) is observed in this FIB section. This is due to image contrast obtained by the interaction of the electron beam with the sample. In a TEM image of an ALH84001 FIB section, denser areas appear darker due to scattering of the electrons in the sample. In addition, scattering from crystal planes introduces diffraction contrast. This contrast depends on the orientation of the magnetite crystal with respect to the direction of the incoming electron beam. Thus, tilting a crystal will cause the gray-level of that crystal to change. As a result, in a TEM image of a sample consisting of randomly oriented crystals, each one will have its own gray-level at a given orientation. In this way discrete magnetites can be distinguished from each other and their carbonate matrix at different tilt angles. Magnetites (e.g., arrows 1–2) and void spaces (e.g., arrows 3–4) are located at the margin of the false colored carbonate crystal. The concentration of magnetites and void spaces at grain boundaries may due to the migration of impurities which occurred during minor carbonate recrystallization. EDX spectrum of false color carbonate shows major Mg, Ca, and Fe with minor Si and Mn. The analysis spot size and acquisition time are \( \approx 100 \) nm and 1000 s, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Fig. 3D. Upper view: TEM image of ‘Texas’ FIB Section 2 extracted from the disk core (see 3A). Carbonate is coarse-grained (\( \approx 1–5 \mu m \) along the longest axis) and displays low porosity. Lower views: expanded view of ROI outlined by red box showing interlocking rhombohedral-shaped carbonate crystals visible at a tilt angle of +30°. Although few magnetites are apparent, this is misleading since at this angle few of the numerous magnetites present were in a strongly diffracting orientation. A rectangular-shaped void, \( \approx 60 \) nm in length, is present in the upper right corner of the view and is shown enlarged on the right. This feature is consistent in both size and shape to negative crystals imaged by TEM (Viti and Frezzotti, 2001). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)
A small amount of the observed pore space (<10% of surface area in the imaged sections) is associated with those grain boundaries (Fig. 3C) along which are also located single stoichiometrically pure Fe₃O₄ crystals (Fig. 5B).

By analogy with terrestrial carbonates, it is unlikely that this texture is primordial, but rather is the result of...
aggrading neomorphism (Folk, 1965), in which diagentic carbonate recrystallization has resulted in an increase in crystal size without a concomitant change in the overall chemistry since fine scale cation zoning is still preserved. During recrystallization, crystallographic imperfections such as void spaces would migrate out to grain boundaries, consistent with our observation that the majority of void spaces are located at grain margins (e.g., Fig. 3C). At the carbonate disk surface the interlocking blocky texture is replaced by a fine-grain matrix as seen in Fig. 1I described previously. In a small number of cases we have interpreted distinctive polygonally shaped voids to represent negative crystals (see Fig. 3D). Cutting through the core carbonate are numerous branching veins (~200 nm to several μm in length) that have fine grained porous texture (Fig. 3C). In contrast to the veins previously described in the outer carbonate core which contain embedded magnetite, these veins do not, being composed of fine grained carbonate intermixed with minor S, although no crystalline sulfides or sulfates were observed.

Fig. 3F. Upper: TEM view of 'Poster Boy' FIB Section 2 (also see 3B). Lower: expanded view of ROI outlined by red box showing discrete nanophase magnetites, some which appear to be associated with voids while others appear to be encased in carbonate. Core carbonate typically displays low porosity (<1 vol.%). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)
In TEM thin sections while some magnetites appear completely encapsulated in carbonate, others are associated with void space. The latter observation has been interpreted as evidence for their formation by thermal decomposition of the host carbonate (Barber and Scott, 2002; Brearley, 2003), since the decarboxylation of siderite to magnetite results in a volume decrease of ~50.5%, due to the higher density of the product magnetite ($\rho_{\text{magnetite}} \approx 5.21$ g · cm$^{-3}$) relative to reactant siderite ($\rho_{\text{siderite}} \approx 3.87$ g · cm$^{-3}$). However, in many cases the void space volume observed is far greater than that which could be accounted for density differences. An alternative explanation is that during carbonate recrystallization grain boundary migration allowed for initially unrelated impurities including void space and magnetites to relocate along grain boundaries, as is observed in terrestrial carbonates (Kennedy and White, 2001; Reid and MacIntyre, 1998).

There have been several reports of individual ALH84001 magnetites having either an epitaxial or topotactic relationship to their host carbonate (Barber and Scott, 2002; Bradley et al., 1996; Brearley, 2003). Although this has again been interpreted as evidence for the partial thermal decomposition of the carbonate matrix we note that such relationships also result as a consequence of low temperature carbonate recrystallization. Numerous observations at low temperature of epitaxial/topotactic overgrowths include quartz on microfibrous opal-CT (SiO$_2$ · nH$_2$O) (Cady et al., 1996) in marine environments, in vivo formation of calcium oxalate (CaC$_2$O$_4$) on calcite (Geider et al., 1996), and growth of aragonite (CaCO$_3$) and calcite on strontium carbonate (SrCO$_3$) from solution (McCauley and Roy, 1974).

3.3.2. Stoichiometrical ‘Pure’ ALH84001 magnetite

In previous studies, we characterized magnetites isolated from entire carbonate disks by chemical dissolution of the carbonate phase using 3M ethanoic acid (CH$_3$CO$_2$H). Compositional analyses by EDX showed that the vast majority of these magnetites (>95%) were stoichiometrically pure Fe$_3$O$_4$ within detection limits (Thomas-Keprta et al., 2000a). While this approach yields an abundant population of magnetites for analysis, all information on their distribution within the host carbonate was lost. In order to preserve this information in this study we performed in situ EDX analyses of individual magnetites present in the ‘Posterboy’ and ‘Texas’ thin sections. Our results indicate that these magnetites share a similar physical size and morphology to those previous characterized and also appear to be stoichiometrically pure Fe$_3$O$_4$. In cases where minor amounts of Mg, Si, and Ca were also observed they were at, or below, levels that could be fully accounted for by spurious X-ray fluorescence from the surrounding carbonate.

---

3 Based on thin film and doped glass standards the minimum level of detection (i.e., >3σ background) for Mg and Mn in 100 nm magnetite crystals, with an integration time of 1500 s, is on the order of 0.05 wt.% for Mg and 0.02 wt.% for Mn.

4 This can occur through either primary or secondary X-ray fluorescence of surrounding carbonate. In the former case, this arises through fluorescence of carbonate that either over or underlies magnetite in the section or through the scattering of the incident electron beam by the magnetite crystal into the surrounding carbonate. In the latter case, Fe K$_\alpha$, X-rays from the magnetite can excite secondary X-ray fluorescence from the surrounding carbonate. Therefore the presence of trace to minor amounts of Mg, Si, and Ca should not be construed to indicate their necessary inclusion as impurities within magnetite, a supposition that is supported by the observation of either the greatly attenuated or the complete absence of Mg, Si, and/or Ca in the subset of magnetites that serendipitously bordered or project into void space.
3.3.3. Impure ALH84001 magnetite

Although the vast majority of the magnetites observed in situ in the ‘Posterboy’ and ‘Texas’ thin sections were chemically pure, there were several notable exceptions. In several cases, Cr at trace to minor levels was observed in a particular magnetite crystal, but absent in the surrounding carbonate (Fig. SC). This is similar to our previous observation of Al and Cr in some magnetites liberated by acid dissolution of ALH84001 carbonate (Thomas-Keprta et al., 2000a). In that instance, Treiman (2003) argued that the Al and/or Cr may have been present as an unobserved Fe-bearing phyllosilicate surface coating. In the present study although we attempted to identify such a magnetite surface phase we were unable to find any evidence to support it on any of the magnetites analyzed in situ within the carbonate.

While both Al and Cr are known to be readily incorporated into the inverse $F_{3}m$ magnetite spinel structure (Karl and Deborah, 2004; Razjigaeva and Naumova, 1992; Thomas-Keprta et al., 2000a), neither has ever been docu-
mented to substitute into the \( R_3^c \) calcite-type carbonate structure. In the absence of any speculative surface coating to explain their presence, those magnetite containing Al and/or Cr could not have formed through thermal decomposition of the surrounding carbonate. To suggest otherwise would require the presence of either a non-existent Al/Cr substituted precursor siderite, or the coexistence of an unknown and indeterminable Al/Cr phase miscible with the precursor carbonate that underwent simultaneous decomposition.

### 3.4. Roxbury siderite

#### 3.4.1. Characterization of unheated Roxbury siderite

Unheated Roxbury siderite was observed to be composed of both coarse and fine-grain components (Fig. 6A). The coarse fraction is characterized by lath-shaped grains ranging in length from \( \geq 0.1 \) to 1 \( \mu \)m, although the upper size limit is likely artificially constrained due to chattering during microtome cutting. In contrast, the fine fraction is characterized by equant particles <50 nm in diameter ranging in geometries from angular to pseudospherical (Fig. 6A). Mixing between the two size fractions was highly variable and sample dependent, giving rise to regions either composed of almost entirely coarse or fine grain carbonate, or an intimate mixture of both. While selected area electron diffraction (SAED) patterns of both coarse and fine grain fractions are consistent with bulk FeCO\(_3\) (Fig. 6A; Table 4), they are compositionally distinct with respect to the degree of cation substitution of Fe by Mg. The fine grained carbonate contains only minor amounts of Mg compared to the coarse grained carbonate which contains major amounts of Mg (Fig. 6A). In both size fractions, however, Mn and Si (in an unidentified amorphous phase) were observed uniformly as minor and trace components respectively (Fig. 6A). No evidence of any Fe-oxide phases was noted.

#### 3.4.2. ‘Slow’ heated Roxbury siderite

‘Slow’ heating of Roxbury siderite resulted in the formation of an optically black product composed of irregular-shaped discrete crystals of magnetite, ranging from ~20 to 500 nm in the longest dimension (Fig. 6B; Table 5). Minor to trace amounts of both Mg and Mn were detected in every magnetite crystal analyzed (Fig. 6C). SAED analysis (Fig. 6B; Table 5). Composition of the ‘slow’ heated product phase (Fig. 6C) is consistent with a (Mg,Mn)-ferrite \(((Mg_{0.5}Mn_{0.5})Fe_2O_4)\) product whose end members are magnetite \((Fe_3O_4)\), magnesioferrite \((MgFe_2O_4)\) and jacobsite \((MnFe_2O_4)\) (Table 5). No
Fig. 4. Upper: schematic representation of the typical carbonate rim structure based on the four ‘Poster Boy’ FIB rim extractions (‘Poster Boy’ Sections 1; 3–5). The inner and outer magnetite-rich rims are not simple radial bands but show a complex network of veins that penetrate both the magnesite rim and the outer core carbonate. These veins are magnetite rich and appear intimately associated with fine-grained Fe-sulfides phases and minor amorphous silica phase. In addition to those magnetites associated with veins, numerous individual magnetites are also distributed throughout the magnesite rims and outer core. As with the vein magnetites these appear chemically pure, that is they are free of cations that characterize the surrounding carbonate, but they are not associated with any sulfides or silica phases (see text for a detailed discussion). Lower: schematic representation of the typical carbonate core structure based on three core FIB extractions, two from ‘Texas’ carbonate and one from ‘Poster Boy’ carbonate (Section 2). In general, the inner core carbonate is composed of multiple interlocked blocky irregularly shaped crystals that are not crystallographically aligned. Rimming the boundaries between these crystals are individual magnetite grains that can account for up to several percent of the volume of the inner core carbonate. Unlike the magnesite band and outer core no magnetite rich veins were observed in inner core sections, however numerous porous fined grained carbonate veins intimately associated with a poorly defined S-rich phase that appears either amorphous or proto-crystalline are observed. These veins run in all orientations and do not correlate with crystallographic boundaries (also see Fig. 3C).
evidence was observed for residual carbonate indicating the decomposition reaction had proceeded to completion, nor was there any evidence for non-ferrous oxides such as periclase (MgO).

3.4.3. ‘Fast’ heated Roxbury siderite

‘Fast’ laser heating of Roxbury siderite under vacuum resulted in a pronounced optical darkening of the original iridescent siderite surface (Fig. 6D).
cross-sections through the altered surface indicated that the laser induced heating penetrated down to a depth of \( \sim 1.0-1.5 \mu m \) (see Fig. 6E). Based on textural differences, the ‘fast’ heated Roxbury siderite can be subdivided into three regions (Fig. 6E). Beginning at the surface and extending down to a depth of \( \sim 400 \) nm (Region 1) the carbonate decomposition has gone to completion to produce closely packed assemblage of Fe-oxides ranging from \( \sim 20 \) to 100 nm in size (Figs. 6E and 6F). In some cases, the temperature excursion created by the laser was sufficient to allowed surface-energy minimization of this Fe-oxide phase resulting in pseudo-spherical morphologies. As with the ‘slow’ heated siderite these Fe-oxides contain variable amounts of Mg but a uniform amount of Mn (Fig. 6F), and SAED patterns implies the formation of both well and poorly crystallized (Mg,Mn)-ferrites (Figs. 6E and 6F; Region 1, Table 5) as defined above. Below this is a second region (Region 2) that extends downward a further \( \sim 800 \) nm in which the carbonate appears to have undergone extensive vesiculation but has not otherwise decomposed as indicated by the absence of Fe-oxides (Fig. 6G; Region 2, Table 4). Finally, below this the carbonate appears indistinguishable from the unheated starting material (Figs. 6A, 6E, Region 3, Table 4).

4. DISCUSSION

Partial thermal decomposition of sideritic carbonate has been proposed as the origin of the nanocrystalline magnetite present within and throughout ALH84001 carbonate disks (Brearley, 2003; Treiman, 2003). This reaction is most commonly formulated as:

\[
3\text{FeCO}_3 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}
\]  
(1)
Would such a process be feasible given the physical and chemical properties of ALH84001 carbonate? Since such a reaction could not have occurred in isolation, we also need to address whether putative thermal decomposition is consistent with the experimental observations of ALH84001 carbonates. Our approach to these issues was to first consider the nature and timing of the heating events that ALH84001 is known to have experienced after carbonate formation and which could have facilitated carbonate decomposition. We argue this provides a natural and convenient way to categorize the various thermal decomposition hypothesis into two groups—those that are subject to kinetic control as exemplified by the model of Brearley (2003) or those that are subject to thermodynamic control.

![Figure 5C](https://example.com/figure5c.png)

Fig. 5C. Upper left: 'Poster Boy' FIB Section 4 showing the location of a Cr-bearing magnetite. Expanded view of the ROI outlined by the red box (upper right) shows the Cr-bearing magnetite embedded in the inner magnetite-rich rim. Lower views: quantitative elements maps (Kα line) for Si, Fe, Cr, and O of the ROI. The rectangular-shaped Cr-bearing magnetite crystal is ~200 nm in length embedded in the inner magnetite-rich rim enriched in Si. No Cr-bearing phases (i.e., phyllosilicates or iron-oxides/hydroxides) surrounded or coated this magnetite. The presence of Cr-bearing magnetite has important implications for thermal decomposition models proposed for the formation of ALH84001 magnetite since this magnetite cannot be the product of thermal decomposition of Cr-free carbonate. We suggest this magnetite is an allochthonous (i.e., detrital) component which became embedded in carbonate during or subsequent to disk formation. ALH84001 magnetites extracted from the carbonate matrix with similar compositions were described previously by Thomas-Keprta et al. (2000a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)
as exemplified by the model of Treiman (2003). We consider both the Brearley (2003) and Treiman (2003) hypotheses first on their intrinsic merits as presented, and second in the light of new observations reported here.

4.1. The ‘ALH84001 Heating Event’

If the partial thermal decomposition of sideritic carbonate is the source of magnetite in ALH4001 disk carbonates, then the nature and distribution of the product magnetites will be a reflection of both the initial carbonate composition and the nature of the heating event from which they formed.

At this stage in is important to make some general remarks on the mechanisms by which reactions in the solid-state are affected. Thermal decomposition of siderite represents the solid-state transformation of an ionic crystal lattice from rhombohedral ($R_3c$) to cubic ($Fd\overline{3}m$) symmetry.

Fig. 5D. Upper left: ‘Poster Boy’ FIB Section 5. Expanded view of the ROI outlined by the blue box shows a magnetite-rich vein cross-cutting outer core carbonate. This vein is not associated with the magnetite-rich rim; it begins at the interface of outer core carbonate and an isolated patch of OPX adhering to the uppermost carbonate surface. Lower views: elements maps ($K_a$-line) for Si, Fe, O, S, Mg, and Mn of the ROI shown in the red box (upper right). The vein is texturally identical to the magnetite-rich rims being composed of nanophase magnetite embedded in a fine-grained carbonate matrix, but contains few Fe-sulfides and is enriched in Si by approximately a factor of three relative to core carbonate. Note Mg is not enriched at the interface of the vein/host carbonate indicating a lack of evidence for cation diffusion (see Section 4). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)
In general solid-state transformations are initiated by a bond redistribution process, in the case of carbonates this is the reversible endothermic dissociation of the carbonate anion $\text{CO}_3^{2-} = \text{O}^{2-} + \text{CO}_2$ (de La Croix et al., 1998), followed by reorganization and remobilization of the isolated anion/cation aggregates thus formed into nascent nucleation sites. At the nucleation sites subsequent growth then occurs preferentially due to the enhanced reactivity of the reactant interface surrounding the nucleating product. This enhanced reactivity is derived in part from the lattice strain existing between reactant and product. Nuclei growth can be envisioned as the progressive advancement of this activated reaction interface into the surrounding reactant phase. Growth will continue until either the interface between the product and reactant is terminated and/or the thermal energy driving the decomposition is dissipated. This process of crystal nucleation and growth is a fundamental assumption in solid state transformations of ionic solids (Galwey and Brown, 1999).

One of the defining characteristics of magnetites embedded in ALH84001 carbonate is their sub-micron size...
distribution. If we assume that the rates of nucleation and growth can be approximated by a Arrhenius-type temperature dependence (see Electronic Annex, EA-1) this would infer that the thermal decomposition of siderite occurred at high temperature so as to facilitate rapid nucleation over crystal growth. Furthermore it is implicit that the heating rate was fast enough to prevent significant carbonate decomposition from occurring before the peak temperature was reached. Otherwise, fewer and larger decomposition products would be expected. Hence, if the magnetites in ALH84001 formed by thermal decomposition, the responsible heating event would have been characterized by a rapid thermal step to high temperature. Given these requirements, and the evidence for multiple shock events experienced by ALH84001, the most probable geological scenario for decomposition would have been during the diabatic propagation of an impact-generated shockwave, either during the impact that ejected the ALH84001 meteorite, e.g., Brearley (2003), or during an earlier pre-ejection impact while ALH84001 remained buried in the Martian regolith, e.g., Treiman (2003). In both cases the shock heating would have been characterized by a near instantaneous rise in temperature followed by a slower monotonic cooling back to ambient. The key difference between the two scenarios is the timescale over which cooling could have occurred. In the first case, cooling would have been rapid and occurred through radiative loss into the vacuum, while in the second case, cooling would have been far slower occurring instead primarily through conduction into the surrounding regolith.

4.1.1. Ejection cooling

It is difficult to tightly constrain the thermal history of ALH84001 immediately following its ejection; nevertheless we can make a reasonable order-of-magnitude estimation by modeling the meteorite as an idealized black body that cools solely by radiative emission (see EA-2). Under such conditions, the time to cool from some initial temperature $T_0$ down to temperature $T_1$ is given approximately by the expression:

$$t_{\text{cooling}} \approx 3.11 \times 10^{11} \cdot \left[ \frac{1}{T_1} - \frac{1}{T_0} \right]$$

From this we estimate that the time for ALH84001 to cool to ambient (~233 K; see EA-2) following its ejection would have been only a matter of hours, corresponding to cooling rates of $\sim 10^{11} \text{ - } 10^{12} \text{ K} \cdot \text{Ma}^{-1}$.

4.1.2. Subsurface cooling

If cooling following a shock heating event had occurred while buried in the Martian regolith then the cooling rate would be a function of both the burial depth and the process by which cooling occurs (e.g., hydrothermal cooling or thermal diffusion). The paucity of hydrous minerals in ALH84001 (Brearley, 1998) implies limited hydrothermal exposure suggesting that heat diffusion would have been the dominant cooling mechanism. In terrestrial impact structures cooling rates in the melt-rich portions are on the order of $10^7 \text{ K} \cdot \text{Ma}^{-1}$, while deeper within the impact structure cooling rates can be much slower, typically $10^2$–$10^3 \text{ K} \cdot \text{Ma}^{-1}$. Several estimations for the cooling histories of the ALH84001 carbonate disks have been made based on cation diffusion studies. Fisler and Cygan (1998) and Kent et al. (2001) have independently determined solid state cation diffusion rates of Mg$^{2+}$ and Ca$^{2+}$ in calcite and magnesite from which they suggest a lower limit for the cooling rate of $\sim 10^2$–$10^3 \text{ K} \cdot \text{Ma}^{-1}$. If the cooling rate were any slower the fine-scale chemical zoning of the carbonates could not have been preserved (Fig. 7A). Most recently, Domenechetti et al. (2007) have used the degree of fractionation of Fe$^{3+}$ and Mg$^{2+}$ between the two non-equivalent octahedral sites, $M1$ and $M2$, in OPX (Fe$^{3+}_{M1}$ + Mg$^{2+}_{M1}$ $\leftrightarrow$ Fe$^{3+}_{M2}$ + Mg$^{2+}_{M2}$) to estimate the cooling rate of the last significant thermal event experienced by the OPX in ALH84001. Their results infer a closure temperature, $T_c$, of $802 \pm 30 \text{ K}$ as a lower limit for the last impact heating event, with a corresponding cooling rate of $\sim 0.1 \text{ K} \cdot \text{day}^{-1}$. This suggests that if partial thermal decomposition of ALH84001 carbonates occurred as a consequence of impact heating during burial, it would have

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</table>

had to have occurred on a timescale of only a few decades or less. In either case to prevent complete, as opposed to partial, decomposition of the carbonate globules, the heating event would have had to have occurred under higher pressure conditions than Mars atmospheric. Assuming a Mars crustal density of $q_{Mars} \approx 3000 \text{ kg} \cdot \text{m}^{-3}$ (McSween, 2002), and a surface gravity of $G_{Mars} \approx 3.72 \text{ m} \cdot \text{s}^{-2}$, the pressure $P$ in bars, at a depth $d$ in meters, can be approximated as $P \approx \frac{q_{Mars}G_{Mars}d}{10}$, Hence a pressure of 10 bars implies a burial depth of $\approx 90 \text{ m}$, while a pressure of 100 bars suggests a burial depth of $\approx 9 \text{ m}$. This is broadly consistent with other estimations of burial depth using cosmic ray exposure data for ALH84001 and the other Martian meteorites (Shuster and Weiss, 2005) that suggest burial depths of at least a few meters for nearly all of their histories. Mikouchi et al. (2006) calculated a burial depth of less than four meters for several nakhlites, which is the original volcanic cooling depth.

4.2. Thermal decomposition models

The two heating scenarios outlined above provide the geological context for the decomposition models developed independently by Brearley (2003) and Treiman (2003). The former is based on carbonate decomposition occurring under “extreme disequilibrium conditions” in which “kinetics are the dominant controlling factor” determining the chemical and physical nature of the magnetites that are formed. This, although never explicitly addressed, is most consistent with the impact event that ejected ALH84001 from Mars. In the latter model, carbonate decomposition occurs “at some depth beneath the Martian surface where the pressure was greater than the atmospheric pressure and the temperature declined slowly.” Under these conditions equilibrium thermodynamics determined the chemical and physical nature of the magnetite formed. In this model, carbonate decomposition occurred prior to ejection, during an earlier epoch, and the eventual ejection event failed to obscure evidence of this earlier thermal episode (as an aside: the Brearley (2003) model is essentially based on inductive reasoning, that is it proceeds from a set of specific observations and experiments to a set of general conclusions. In contrast the Treiman model is based on deductive reasoning, that is, the fundamental postulates of thermodynamics are used to extrapolate the outcome of a single specific event).

It should be noted that these models are necessarily contradictory; that is they cannot both have occurred since application of one model negates the applicability of the other. Indeed as Brearley (2003) noted, “equilibrium phase diagrams have only limited relevance… the kinetics of the reaction, rather than the thermodynamics, control the phase and their compositions.” It is also necessary in the subsequent discussion to bear in mind in each model the key question is not whether a siderite-magnesite-[calcite] carbonate can undergo preferential decomposition of the sideritic component, since to some extent this may well be true. Rather the question is can the sideritic component of such a mixed carbonate undergo decomposition to the complete exclusion of the magnesite–calcite components, since this is what would be necessary to explain the observations of ALH84001 carbonates. The lack of any evidence whatsoever for the partial or complete thermal decomposition of the magnesite and calcite-rich components of ALH84001 carbonates requires that any proposed thermal decomposition mechanism must be tightly limited to the siderite-rich

Fig. 6B. Upper: TEM view of an ultramicrotome section of Roxbury siderite after heating to 848 K using the LSQT method of Golden et al. (2006). The heating rate was 1 K · min$^{-1}$ (i.e., ”slow” heating) with the peak temperature being maintained for 24 h (see Methods section). The grain size ranges from $\approx 20$ to 200 nm. Lower: SAED pattern of heated Roxbury siderite shown above. Measured $d$-spacings indicate the siderite has converted completely to magnetite.

Although ALH84001 probably formed as a cumulate in an intrusion several 10s of kilometers in depth (McSween and Treiman, 1998), its shock history suggests that it was later excavated to much shallower depths.
carbonate only. Consequently, we address the merit of each model separately, and consider only those aspects of each model that relates specifically to chemical and physical nature of magnetites formed from carbonate decomposition.

4.2.1. Kinetically controlled carbonate decomposition – Brearley (2003) model

The key aspects, as relevant to the discussion herein, of the hypothesis proposed by Brearley (2003) can be condensed into three main points:

1. ALH84001 underwent a rapid heating and cooling event as a consequence of a shock event.
2. The most sideritic component of the carbonate disks “...decomposed preferentially and at a significantly lower temperature than either the magnesite, calcite, or rhodochrosite component in solid solution.”
3. The timescale for this thermal event was short enough to prevent any re-equilibration of the decomposition products or compositional zoning patterns remaining in the residual carbonate.

Critical to this hypothesis is the supposition that under conditions characterized by a “high degree of disequilibrium,” partial decomposition of siderite carbonate would favor the formation of pure magnetite. The rational is that “under disequilibrium conditions, the earliest phase that forms is the one which is kinetically the easiest to nucleate, in this case, a simple binary oxide [i.e., magnetite] rather than a more complex solid solution [i.e., magnetite-magnesioferrite].” Several problems, however, exist with the Brearley (2003) hypothesis, particularly with over-generalizations that are made on the basis of limited or ambiguous experimental data.

4.2.1.1. Preferential decomposition of siderite solid solutions. Brearley (2003) argues that a substantial body of experimental data exists to support the contention “that a complex carbonate solid solution can undergo progressive decomposition, such that one component in solid solution breaks down without the entire phase decomposing.” By way of example, “the behavior of ferromanganan dolomite (Iwafuchi et al., 1983) and carbonates in the dolomite-ferroan, dolomite-ankerite series (Milodowski et al., 1989) [which] exemplify the decomposition behavior of complex carbonate solutions,” is cited. In both studies “…the decomposition of dolomite and ankerite is complex and involves distinct stages of CO2 evolution, indicating that decomposition is taking place in different stages.” From this is argued that both studies “…demonstrate that preferential decomposition of one of two carbonate components (i.e., FeCO3, MgCO3) can occur, leaving the third (CaCO3) intact.”

We argue, however, that the relevance of this example is in fact limited and more applicable experimental results need to be considered. In the decomposition studies of ankerite-dolomite solid solutions (Fe0.7xMg1−x/3Ca(CO3)2; 0 ≤ x ≤ 0.7) discussed above, decomposition was interpreted as proceeding in a series of three consecutive stepped reactions, with the first step involves the preferential decomposition of the Fe0.7xMg1−x/3Ca(CO3)2 ‘component’ in the presence of the CaCO3 ‘component,’ that is:

\[
\text{Fe}_x\text{Mg}_{1−x}\text{Ca}(\text{CO}_3)_2 \rightarrow \frac{x}{2} \text{MgFe}_2\text{O}_4 + \left(1-\frac{3x}{2}\right)\text{MgO} + \text{CaCO}_3 + \left(1-\frac{x}{2}\right)\text{CO}_2 + \frac{x}{2}\text{CO}
\]

(3)

for (2/3 ≤ x ≤ 7/10),

\[
3\text{Fe}_x\text{Mg}_{1−x}\text{Ca}(\text{CO}_3)_2 \rightarrow \text{Mg}_x\text{Fe}_{3−x}\text{O}_4 + 3\text{CaCO}_3 + 2\text{CO}_2 + \text{CO}
\]

(4)

While it is true that this represents an example of a preferential decomposition of one component (Fe, Mg) of a solid solution carbonate in the presence of another (Ca), it in and of itself does not address the more relevant question as to whether the sideritic component of a siderite-magnesite solid solution would also preferentially decompose (under disequilibrium conditions). The reason that calcitic component of ankerite-dolomite solid solution does not undergo decomposition with the siderite-magnesite solid solution is that neither siderite nor magnesite can form a complete solid solution series with calcite. In contrast,
Fig. 6C. Upper views: TEM image and accompanying EDX spectra (1000 s acquisition time) of a grouping of magnetite crystals produced by the ‘slow’ heating of Roxbury siderite. Three magnetite crystals labeled ‘A’, ‘B’, and ‘C’ (outlined in green, blue, and red) are highlighted. Magnetites ‘A’ and ‘C’ contain only minor Mg relative to magnetite ‘B’, while minor Mn is present in all three grains in approximately the same concentration. Lower views: element maps (Kα line) of Fe, Mg, Ca, and Mn for the entire grouping of magnetites shown in the upper TEM view (red box), illustrating the compositional heterogeneity of Mg in the magnetite product (color bar to right of map represents the number of counts per pixel). Since the observed cation variations mirror those of the unheated Roxbury siderite (see 6A) there is no significant cation diffusion occurring during the ‘slow’ heating thermal decomposition. That is, the cation composition of a given magnetite grain simply reflects the cation composition of the progenitor carbonate grain from which it formed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)
siderite–magnesite solid solutions do form a complete series between end members. Hence, the decomposition of ankerite-dolomite solid solution is an example of a spinodal decomposition in which a phase transform/separation to calcite and a siderite–magnesite solid solution occurs prior to nucleation and growth of the decomposition product phases. In fact, in these studies the siderite–magnesite solid solution that initially decomposes forms a mixed cation spinel which would appear to directly conflict with the argument for which this reaction was proposed to support, namely that of the exclusive decomposition of the sideritic component of a siderite–magnesite solid solution to form pure magnetite. The data from these experiments show that pure magnetite does not result, rather, a mixed Fe–Mg spinel is the product.

While the kinetics of the thermal decomposition of siderite and its solid-solutions have been extensively studied (Dhupe and Gokarn, 1990; Jagtap et al., 1992; Kubas and Szalkowicz, 1971; Zakharov and Adonyi, 1986) great care needs to be taken in interpreting the results of such studies since there are many discrepancies between datasets. The reasons appear to be two fold: first, reaction kinetics are sensitive to the physical parameters of the sample, e.g., degree of crystallinity, surface area, presence of impurities, particles size, and the degree of compaction or porosity. Second, non-isothermal decomposition traces alone can typically be fitted, with good correlation coefficients, to any number of kinetic models. Consequently we consider here the work of Gotor et al. (2000) who have utilized both linear heating rate (TG) and constant rate thermal analysis (CRTA) procedures to investigate the decomposition kinetics of both a pure ‘synthetic’ siderite and a ‘natural’ Mg-bearing siderite (\(\text{Fe}_{60.162}\text{Mg}_{0.303}\text{Mn}_{0.052}\text{Ca}_{0.022})\text{CO}_3\)) under identical conditions. Their results indicated that the thermal decomposition reaction of pure siderite followed an Avrami-Erofeev A2 random nucleation and growth model, while the natural Mg-bearing siderite instead followed an \(F_1\) unimolecular decay model. Fig. 7B shows...
the model decomposition curves, calculated from the results of Gotor et al. (2000) for both pure and natural siderites under heating rates of 0.52, 5.2, and 52 K·min⁻¹. Several important observations can be drawn from the experiments:

- For both pure and natural siderites at all heating rates the onset of decomposition occurs at temperatures that greatly overstep the thermodynamic stability limit predicted for both pure siderite and magnesite–siderite solid solutions.
- The kinetic effect on the stability of siderite as a consequence of magnesium substitution is at least an order of magnitude larger than would be predicted from thermodynamic equilibrium arguments alone.
- Mg-bearing siderite does not decompose in two or more separate stages in which preferential decomposition of the siderite component occurs first.

From the first observation it is clear that even at heating rates that are far slower than those associated with shock heating, decomposition still occurs under conditions that are far from equilibrium. If this is true then the all the carbonate decomposition studies listed in Table 6 can be considered pertinent to the origin of magnetite in ALH84001 carbonate. Results from these investigations all show that decomposition of magnesite–siderite solid solution carbonate under a variety of atmospheres and a range of heating regimes invariably produces an impure Mg-substituted magnetite in which there is little to no evidence of the preferential decomposition of the siderite component of solid solution. While Brearley (2003) suggests “that Fe-rich phases with little or no Mg can be formed as metastable phases during the very earliest stages of decomposition,” it is unclear how this is relevant to magnetite in ALH84001 carbonate for two reasons: first, the magnetites in ALH84001, while sub-micron in size, are still well beyond the size associated with primary nuclei (as demonstrated by their well defined crystal faceting); and, second, since at least 50% of the volume in the magnetite rims of ALH84001 carbonate is accounted for by magnetite and if these magnetites were formed from thermal decomposition, this would require nearly 70% of the carbonate...
initially present in the rims to have decomposed.\textsuperscript{10} A reaction having gone to this extent cannot be construed as being in its initial stages. To be able to rapidly decompose nearly 70\% of a siderite-magnetite carbonate in a near instantaneous, highly non-equilibrium, decomposition event and expect the product to be essentially pure magnetite is highly implausible. The Fe/Mg ratio of the decomposition products would more likely be similar to the Fe/Mg ratio of the initial carbonate and show little, if any, chemical fractionation except lost of CO and CO\textsubscript{2}, especially given the results of pulse laser heating experiments on mixed composition Roxbury siderite, which are able to duplicate and even exceed impact shock heating rates and yet always produced impure magnetites (see Results section ‘Roxbury Siderite’; also see Table 6).

\textsuperscript{10} Assuming carbonate decomposes via the reaction \(3\text{FeCO}_3 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}\) then the volume ratio of carbonate to magnetite \((V_{\text{ratio}})\) when the extent of reaction is \(\alpha\) \((0 \leq \alpha \leq 1)\) is given by \(V_{\text{ratio}} = \frac{\alpha V_{\text{carb}}}{1 - \alpha V_{\text{magn}}}\), where \(V_{\text{carb}}\) and \(V_{\text{magn}}\) are the molar volumes of carbonate and magnetite respectively. Assuming \(V_{\text{carb}} \sim 2.9\,\text{cm}^3\) and \(V_{\text{magn}} \sim 4.5\,\text{cm}^3\) and solving for \(\alpha\) when \(V_{\text{ratio}} \sim 1\), gives the extent of reaction as \(\sim 67\%\).
of (Fe$_{0.1}$Mg$_{0.9}$)CO$_3$ was 0.25010 nm, while that for (Fe$_{0.8}$Mg$_{0.2}$)CO$_3$ was 0.25227 nm.

Neither observation provides compelling evidence for the preferential decomposition of siderite in a solid solution carbonate to form pure magnetite. In the first case, lacking any data pertaining to the fraction of carbonate that underwent decomposition, the spinel product formed could have had any composition between Fe$_3$O$_4$ and Mg$_{0.3}$Fe$_{2.7}$O$_4$ (see EA-3). While in the second case, the 0.25010 nm line reported by Koziol (2001) for the $d_{006}$ line of magnetite formed from the decomposition of (Fe$_{0.1}$Mg$_{0.9}$)CO$_3$ is below any reported value of any documented (Mg,Fe)-spinel, and most likely assignable to the $d_{006}$ line of the undecomposed starting carbonate (see EA-3).

4.2.2. Thermodynamic carbonate decomposition – Treiman model

Treiman (2003) has proposed a “comprehensive abiotic hypothesis” to explain the presence of fine-grained magnetite embedded in ALH84001 carbonate disks that “invokes high pressures, significant time for chemical reactions and chemical equilibria.” The geological context for the hypothesis assumes that while ALH84001 was buried at “some depth beneath the Martian surface”, it was subjected to an impact shock (I3 event$^{11}$) that resulted in it being heated “rapidly to super ambient conditions,” resulting in the thermal decomposition of the most sideritic carbonate according to the reaction:

$$3\text{FeCO}_3(\text{Fe}–\text{Mg solid solution}) \rightleftharpoons \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}$$  \hfill (5)$$

The ALH84001 rock subsequently cooled back slowly to ambient temperature over “a relatively short time geologically... less than centuries.” Under these conditions the size distribution of magnetites is determined by kinetic factors since the nearly instantaneous temperature increase associated with passage of the shock wave results in carbonate decomposition under conditions far from equilibrium. The chemical composition of these magnetites, is however, determined subsequently by thermodynamic constraints during cooling where re-equilibration of magnetite with the host residual carbonate is presumed to have occurred. The conditions of such re-equilibration implicitly requires a closed system in which the 2CO$_2$ + CO gas phase evolved during the initial decomposition is not dissipated or diluted,

$^{11}$ I3 event in shock chronology proposed by Treiman (1998).

Fig. 7A. Length scale, $x$, over which Mg$^{2+}$ heterogeneities in calcite (CaCO$_3$) would be homogenized by thermal diffusion–adapted from Kent et al. (2001). The thermal event that drives the diffusion is assumed to be characterized by an instantaneous rise in temperature to some peak value, followed by slow monostatic cooling back to ambient. Diffusion lengths for peak temperatures $T_0$ ranging from 500 to 900 K are shown by the solid lines in the plot. For a given initial cooling rate denoted on the abscissa axis, the diffusion distance, $x$, can be determined by tracing a vertical line from the abscissa up to the intercept with the solid line corresponding to the given peak temperature. From this intercept a horizontal line traced to the ordinate axis gives the diffusion distance, $x$, ranging from 500 to 900 K are shown by the solid lines in the plot. From this intercept a horizontal line traced to the ordinate axis gives the diffusion distance, $x$, ranging from 500 to 900 K are shown by the solid lines in the plot.

Fig. 7B. Decomposition kinetics of pure and Mg-substituted siderite as a function of linear heating rates. The two curves corresponding to a heating rate of 0.52 K·min$^{-1}$ are the best fits to the experimental data of Gotor et al. (2000) corresponding to an Avrami-Erofeev A2 random nucleation and growth model for pure siderite, and an F$_1$ unimolecular decay model for the Mg-substituted siderite. The curves corresponding to heating rates of 5.2 and 52 K·min$^{-1}$ are extrapolated using these kinetic models and the pre-exponential factors ($A$) and activation energies ($E_{\text{Act}}$) calculated by Gotor et al. (2000). For pure siderite $dx = \sqrt{\log{(1-x)} \cdot A \cdot \exp\left(-\frac{E_{\text{Act}}}{RT}\right) \cdot dt}$ where $A = 7.88127 \times 10^8$ s$^{-1}$ and $E_{\text{Act}} = 106$ kJ·mol$^{-1}$, and for natural siderite $dx = (1-x) \cdot A \cdot \exp\left(-\frac{E_{\text{Act}}}{RT}\right) \cdot dt$ where $A = 2.52625 \times 10^9$ s$^{-1}$ and $E_{\text{Act}} = 192$ kJ·mol$^{-1}$. Numerical solutions for these differential equations were determined using the Adams–Bashforth–Moulton predictor-corrector method (Mathews and Fink, 2004). The effect of Mg substitution in siderite has a profound consequence on the decomposition temperature and is substantially larger than that predicted based solely on equilibrium thermodynamics.

Origins of Magnetite in ALH84001 6663

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Table 6

Previous decomposition studies of natural and synthetic siderites.

<table>
<thead>
<tr>
<th>Composition of Unheated Carbonate</th>
<th>Atmosphere</th>
<th>Decomposition Temperature and Product Phases</th>
<th>References</th>
</tr>
</thead>
</table>
| Synthetic solid solution siderite (0.0 to 100.0 mol.% FeCO₃) | O₂         | • 770 °C
• Solid solutions from 0–66.6 mol.% FeCO₃ \(\Rightarrow\) magnesioferrite spinel (MgFe₂O₄) and MgO
• Solid solutions from 66.7 to 100 mol.% FeCO₃ \(\Rightarrow\) magnesioferrite spinel (MgFe₂O₄) and Fe₂O₃ | (Chai and Navrotsky, 1996a) |
| Ankerite solid solution \(^a\) Ca(FeₓMg₁₋ₓ)(CO₃)₂ where 0 < x < 1 | O₂         | • 770 °C
• CaO
• MgO
• Ca₂Fe₂O₅ | (Chai and Navrotsky, 1996b) |
| (Fe₀.₇Mg₀.₃)CO₃ | Vacuum     | • Decomposition begins 452 °C
• Mixed Mg–Fe oxides
• No MgO | (Gotor et al., 2000) |
| Mixed cation FeCO₃ (1) 95.3 mol.% FeCO₃, 4.2 mol.% MnCO₃, 0.4 mol.% MgCO₃ (2) 85.5 mol.% FeCO₃, 4.0 mol.% MnCO₃, 7.6 mol.% MgCO₃, 0.9 mol.% CaCO₃ (3) 81.7 mol.% FeCO₃, 6.4 mol.% MnCO₃, 9.5 mol.% MgCO₃, 1.5 mol.% CaCO₃ | N₂ and O₂ | • Decomposition begins at lower \(T\) in N₂
• In N₂: mixed Mg–Mn ferrites
• In O₂: mixed Mg–Mn ferrites and hematite
• Spinel impurities increase with increasing carbonate impurities | (Gallagher and Warne, 1981b) |
| Mn-bearing natural siderite | Air        | • 480–530–700 °C (°C)
• Hematite (initial)
• Mn-ferrite (final) | (Hakonardottir et al., 2002) |
| Siderite: 79.16 wt.% FeCO₃, 1.04 wt.% MnCO₃, 16.40 wt.% MgCO₃, 3.76 wt.% Fe₂O₃, 0.43 wt.% CaCO₃ | N₂ and O₂ | • 0 to 1000 °C
• N₂: major impurities incorporated into the spinel product
• O₂: no spinel intermediate phases detected | (Gallagher and Warne, 1981a) |
| Siderites: Approximate mole fraction Fe (Fe/(Fe + Mn + Mg + Ca)) (1) 0.0 (2) 0.3 (3) 0.6 (4) 0.7 (5) 0.8 (6) 0.9 | N₂         | • Onset and Peak Temperature of Decomposition (°C):
• Mixed composition products from mixed composition siderite
  o Ferroan magnesite \(\Rightarrow\) Mg-ferrite
  o Mn–Mg-siderite \(\Rightarrow\) Mn-Mg-Fe-oxides | (Dubrawski, 1991b) |
| Bakal siderite (impure) | Air        | • Decomposition begins 350 °C
• MgFe₂O₄ | (Bagn et al., 1974) |
| Siderite: (Fe₀.₇Mn₀.₃Mg₀.₀₂Ca₀.₀₂)CO₃ | Air        | • Magnesiowustite
• 700 °C
• Mn-magnetite | (Isambert and Valet, 2003) |
| Ankerite: (CaMg₂Fe₃Mn)(CO₃)₂ | CO₂ (1 atm) | • Siderite, 500–700 °C
• Ankerite, 600–800 °C
• Significant amounts of Mn and Mg in ferrites | (Cohn, 2006) |
Table 6 (continued)

<table>
<thead>
<tr>
<th>Composition of Unheated Carbonate</th>
<th>Atmosphere</th>
<th>Decomposition Temperature and Product Phases</th>
<th>References</th>
</tr>
</thead>
</table>
| Copper Lake Siderite (~0 to 21 mol.% Mg) | Impact shock CO₂ (10⁻³ torr) 30 to 49 GPa | • 740 °C
  • Ferrites with range in composition (~0 to 21 mol.% Mg) | (Bell, 2007) |
| Siderite: Fe₀.₇₉Mn₀.₁₂Mg₀.₀₇Ca₀.₀₂ | Laser under vacuum 8.4 to 25.9 GPa | • Mn-“magnetite-like” | (Isambert et al., 2006) |
| FeCO₃, Ca-siderite (70–90 wt.% series) has not been reported. | | | |
| (1a,b) Siderite | N₂ and O₂ | • Decomposition begins at lower T in N₂: (1a) N₂ 450–550 °C
  (1b) O₂ increased by ~50 °C over 1a | (Ware and French, 1984) |
| (2a,b) Magnesite | | (2a) N₂~500–600 °C
  (2b) O₂ increased by ~70 °C over 2a | |
| (3a,b) Calcite | | (3a) N₂~680–780 °C
  (3b) O₂ increased by ~150 °C over 3a | |
| Siderite (>90 wt.% FeCO₃) | N₂, O₂, CO₂, H₂O | • Siderite decomposition T increases proportional to extent of substitution by Mg, Mn, and Ca | (Hurst et al., 1993) |
| Ca-siderite (70–90 wt.% FeCO₃~10 wt.% CaCO₃) | | • Decomposition T decreases with increasing FeCO₃ | |
| Mn-siderite (up to 28 wt.% MnCO₃) | | • Non-linear decrease in decomposition T with increase in partial pressure H₂O | |
| Mg-siderite (10–30 wt.% MgCO₃) | | • Decomposition T increases non-linearly with increasing CO₂ | |
| High Mg-siderite (30–60 wt.% MgCO₃) | | o Low partial pressure (~25 kPa) CO₂ produces increase in decomposition T (e.g., in N₂,FeCO₃ decomposes at 375 °C; in CO₂, FeCO₃ decomposes at 500 °C) | |
| Ferroan magnesite (>60 wt.% MgCO₃) | | | |

* Results typical for decomposition of carbonates in ankerite–dolomite solid solution series. Compositions of phases formed are variable, determined by compositions of the precursor carbonates. Formation of chemically pure Fe₃O₄ by thermal decomposition of carbonates in this series has not been reported.

and furthermore the fO₂ is solely defined by this 2CO₂ + CO gas phase. Unfortunately, the merit of the Treiman (2003) hypothesis is undermined by the use of erroneous or questionable thermodynamic data and the application of incongruous experimental results as discussed below.

4.2.2.1. Siderite stability field. The thermodynamic stability field of siderite is calculated incorrectly in Treiman (2003) and this subsequently affects many of the later calculations. In a closed system, the decomposition of siderite according to reaction (5) will be a function of the intensive variables of pressure and temperature, and if the siderite is not pure, but rather present as a solid solution, its activity as well. In calculating the siderite stability field Treiman (2003) used the thermodynamic software package THERMOCALC (Holland and Powell, 1998; Powell et al., 1998) in combination with a regular solid solution activity-composition model (Chai and Navrotsky, 1996a) to describe the siderite-magnesite solid solution series. Regrettably, the results of these calculations are incorrect since it appears that no consideration was made to address the absence of an appropriate equation-of-state (EOS) for CO in the THERMOCALC package, which only includes a compensated Redlich-Kwong EOS to determine fugacities for CO₂ and H₂O. Hence, all the calculations in Treiman (2003) relating to siderite decomposition involving the presence of a CO gas phase product are wrong. Using the most recent version of the thermodynamic dataset used by THERMOCALC v3.26 (and hence for referred to as HP98(12)), in combination with the Peng–Robertson–Gasem cubic EOS (Gasem et al., 2001), and assuming Lewis Randall fugacity mixing rules (Lewis and Randall, 1961), the correct siderite stability P–T plot is shown in Fig. 7C. From this it is apparent that the correct thermodynamic decomposition temperature of siderite is actually considerably higher than that shown Figs. 3 and 4 of Treiman (2003) (a more comprehensive description of the relevant thermodynamic calculations can be found in EA-4).

4.2.2.2. Composition of magnesioferrite–magnetite solid solutions. The equilibrium extent of Mg²⁺ substitution in the magnetite product produced from the decomposition of siderite carbonate can be addressed thermodynamically by casting an Mg²⁺-substituted magnetite as a solid solution between magnesioferrite and magnetite proper, that is:

12 http://www.earthsci.unimelb.edu.au/tpg/thermocalc
Mg$_x$Fe$_{3-x}$O$_4 \rightarrow x \cdot MgFe_2O_4 + (1-x) \cdot Fe_3O_4$  \quad (0 \leq x \leq \frac{1}{3})

Under the conditions of siderite decomposition proposed by Treiman (2003) two thermodynamic methods are developed to provide limits to the mole fraction of magnesioferrite present in ALH84001 magnetites. Both approaches appear to yield similar results, namely that the mole fraction of magnesioferrite is expected to be very low and probably undetectable by TEM/EDX. This is, however, misleading as both approaches use either erroneous or logically inconsistent data and the similarity in the results for each is simply coincidental, as discussed in EA-5, where we show that because of the omission of an equation of state in the THERMOCALC package used by Treiman (2003), the calculated minimum concentration of Mg-spinel component in the Fe-spinel decomposition product is $\sim 3 \times$ higher than estimated by Treiman (2003) and would be detected by TEM/EDX analysis.

As shown in EA-5, the use of data from multiple sources in the THERMOCALC treatment of oxygen fugacity also produces a significant underestimation of the activity of the magnesioferrite component in the resulting decomposition product. A more consistent database predicts that the magnesioferrite component would be much higher and detectable by TEM/EDX techniques.

4.2.2.3. Where is the graphite? Metastability of CO$_2$–CO gas mixture and the formation of graphite. Central to the Treiman (2003) hypothesis is that the decomposition of siderite occurs in a closed system via reaction (1) to produce magnetite and a 2CO$_2$ + CO gas phase. It is the presence of this 2CO$_2$ + CO gas that allows re-equilibration of Mg$^{2+}$ between magnetite and carbonate via the following reaction:

$$2FeO_4 + 3MgCO_2 = 3MgFe_2O_4 + 2CO_2 + CO$$  \quad (7)

Additionally it is also used to define the $f_O$ conditions for the reduction of magnesioferrite to magnetite proper and periclase via the following reaction:

$$3MgFe_2O_4 \rightleftharpoons 2FeO_4 + 3MgO + \frac{1}{2}O_2$$  \quad (8)

Nevertheless thermodynamically under the reaction conditions presumed for siderite decomposition (“pressures on the order of tens to hundreds of bars” and temperatures in the range of 600–800 K) CO would be unstable with respect to disproportionation via the Boudouard reaction:

$$2CO = CO_2 + C$$  \quad (9)

Consequently, the thermodynamically favored reaction for thermal decomposition of sideritic carbonates is:

$$6FeCO_3 \rightleftharpoons 2FeO_4 + 5CO_2 + C$$  \quad (10)

Fig. 7D shows the $P-T$ phase stability curves for both pure siderite and siderite–magnesite solid solutions calculated using thermodynamic data from THERMOCALC and assuming the regular solid-solution mixing model described previously for siderite-magnesite solid solutions. While Treiman (2003) does note that formation of a graphite phase ought to be one of the products of siderite decomposition under conditions approaching equilibrium, it is argued that “formation of graphite, the thermodynamically stable phase, would be kinetically hindered.” In other words, although the Boudouard reaction is thermodynamically spontaneous, graphite deposition in the absence of a catalyst is minimal due to the high activation barrier. For practically all laboratory investigations of siderite decomposition, it is true that in most cases experiments are conducted over time intervals of less than a few days. Hence, while French and Eugster (1965) noted
that “it is possible that rates of equilibration between graphite and gas are slow enough so that a gas phase with metastably low CO₂/CO ratios could be maintained without precipitation, particularly at low temperatures” their experimental data indicated “that equilibrium is attained through precipitation of graphite during runs of long (two weeks) duration.” Tamura and Tabata (1990) showed conversion efficiencies near 100% using cation excess magnetite (Fe₂.₈₈₇O₄) as a catalyst in CO₂ to form graphite at 563 K. It is should also be noted that the use of CO₂–CO gas furnace mixtures to fix fO₂ in mineral equilibria investigations are usually restricted to temperatures above ~1200 K due to problems associated with graphite precipitation (Huebner, 1975; Jurewicz et al., 1993). These studies all suggest that graphite should be one of the decomposition phases in ALH84001, if siderite was decomposed to form magnetite.

Although no exact analogues to ALH84001 carbonate have been identified in the terrestrial geological record, ancient (>3.5 Ga) secondary carbonate deposits occurring in vein fractures of rocks forming the in 3.8 Ga old Isua supracrustal belt in southern West Greenland do provide an interesting comparison (Zuilen et al., 2002). These carbonate deposits are intimately associated with the presence of magnetite and graphite inclusions. Carbon isotope analyses indicate the parentage of the graphite to be derived from the carbonate, and it is generally accepted that both the magnetite and graphite formed by the disproportionation of Fe²⁺-bearing carbonates at high temperature as shown in reaction (10) (Zuilen et al., 2002).

Since no graphite has ever been observed in us in any ALH84001 carbonate, if we assume the magnetite formed by thermal decomposition then the time available for the attainment of thermodynamic equilibrium would have had to have been short, perhaps on the order of weeks (or less depending on the ability of magnetite to promote precipitation of graphite through surface catalysis). This is a far more rigorous constraint that the "...less than centuries" as proposed by Treiman (2003), and would arguably be too short to allow any significant degree of chemical equilibration between magnetite and carbonate in ALH88001.  

4.2.2.4. Siderite–magnetite stability and oxygen fugacity. In the thermodynamic model of siderite decomposition it has been implicitly assumed that the system is closed. Although not specifically a criticism of the Treiman (2003) hypothesis it is useful at this point to consider the consequences if this were not the case. Specifically let us consider the situation in which the fO₂ is influenced by the external environment, as is often the case in geological settings. Since the thermal decomposition of siderite to magnetite involves a change in oxidation state of the Fe cation we can expect there to be only a limited range of fO₂ values for which both siderite and magnetite can coexist. This should be contrasted with the analogous decompositions of magnetite to periclase or calcite to lime which are fO₂ invariant since they involve no changes in redox. In order to explicitly determine the fO₂ dependence of the partial decomposition of siderite to magnetite we need to consider the stability field of siderite in P – T – fO₂ space, which is defined by the bivariant reaction surfaces representing oxidation to either hematite or magnetite, and the interconversion between hematite and magnetite, that is:

\[
\begin{align*}
2\text{FeO}_3 + 4\text{CO}_2 &= 4\text{FeCO}_3 + \text{O}_2 \\
2\text{FeO}_3 + 6\text{CO}_2 &= 6\text{FeCO}_3 + \text{O}_2 \\
6\text{FeO}_3 &\Rightarrow 2\text{Fe}_3\text{O}_4 + 6\text{C} + 5\text{O}_2 \\
6\text{FeO}_3 &\Rightarrow 4\text{Fe}_3\text{O}_4 + 6\text{C} + 5\text{O}_2
\end{align*}
\]

From inspection of reactions (12) and (13) it is can be seen that their equilibrium surfaces in P – T – fO₂ space will intersect on the graphite buffer surface defined by the reaction:

\[
\text{C} + \text{O}_2 = \text{CO}_2
\]

To visualize these relationships it is convenient to consider 2-D slices through the relevant region of P – T – fO₂ space perpendicular to one of the axis vectors, in our case this will be pressure. Under isobaric conditions the bivariant reaction surfaces for reactions (11–14) appear as univariant curves in T – fO₂ space. Provided that the partial pressure of O₂ defined by the value of fO₂ is negligible in comparison to the total gas pressure of the system, the position of the univariant curves defined by reactions (11–14) can be calculated by equating the respective thermodynamic equilibrium constants to the Gibbs free energy of reaction, that is:

\[
f_{\text{O}_2} = \exp \left[ \frac{\Delta G_{\text{eq}}^{\text{rxn}}}{R \cdot T} \right]
\]

The Gibbs phase rule \(\omega = \eta + r - \phi - r\) establishes a relationship between the variance (\(\omega\)) of a thermodynamic system and the number of components (\(\eta\)), the number of intensive variables (\(r\)), the number of phases (\(\phi\)) and the number of independent chemical reactions that are occurring in the system (\(r\)). In the Fe–C–O system there are three components (i.e., Fe, C, and O) so \(\eta = 3\), while in P – T – fO₂ space there are three intensive variables (i.e., \(P, T, f_{\text{O}_2}\)) and so \(r = 3\). Thus the Gibbs phase rule can be rewritten as \(\omega = 6 - \phi - r\) – r. For reactions (11, 12) we have two solid phases in equilibrium with a gas so \(\phi = 3\), and setting \(r = 1\) we find the variance \(\omega = 2\) defining a surface in P – T – fO₂ space. Under isobaric conditions in T – fO₂ space the number of intensive variables is reduced to \(\nu = 2\) (i.e., \(T\) and \(f_{\text{O}_2}\)) so that \(\omega = 1\) defining a univariant curve. In the case of reaction (13) before applying the phase rule it must necessary to realize that we are implicitly assuming the presence of an imaginary or inert gas is also present in the system otherwise we would not be able to vary the partial pressure of O₂ since it would be the only gas in the system and hence would always be at the system pressure \(P\). We account for this imaginary or inert gas by increasing the number of components necessary to describe the system, i.e., \(\eta = 3 + 1 = 4\). Since we have three solid phases in equilibrium with a gas we have \(\phi = 4\) and \(r = 1\). Now applying the phase rule we obtain a variance \(\omega = 4 + 3 - 4 - 1 = 2\) in P – T – fO₂ space and \(\omega = 1\) in T – fO₂ space. Finally for reaction (14) since C is absent the number of components is two (i.e., Fe and O) + the imaginary or inert gas necessary allow variation of the partial pressure of O₂ hence \(\eta = 3\). There are two solids and a gas phase described by a single reaction so \(\phi = 3\) and \(r = 1\). Hence from the phase rule the variance \(\omega = 3 + 3 - 3 - 1 = 2\) in P – T – fO₂ space and \(\omega = 1\) in T – fO₂ space.
Fig. 7E. Siderite stability field in $P$–$T$–space, using thermodynamic data from the updated Holland and Powell (1998) database (THERMOCALC Ver. 3.26) and assuming a Peng–Robinson–Gasem EOS for gas phase species (Gasem et al., 2001). Each plot represents a 2-D slice through $P$–$T$–space under isobaric conditions corresponding to pressures of 1, 10, and 100 bars, respectively. The siderite stability field is indicated by the magenta plus gold shaded wedge (shown outlined by the black dashed line in the middle plot) that splits the hematite and magnetite fields. The presence of siderite coexisting with magnetite in the absence of graphite occupies a restricted region in $T$–$P$–space defined by the curve, which defines the upper limit of the siderite stability field. This line connects the two invariant points in $T$–$P$–space corresponding at lower temperature to the coexistence of siderite + magnetite + hematite + gas, and at higher temperature to siderite + magnetite + graphite + gas. Note that the siderite stability field is itself divided into the magenta and gold shaded regions by the black line corresponding to the equilibrium $2\text{CO} = \text{C} + \text{CO}_2$. (For interpretation of the references to color in this figure legend, to reader is referred to the web version of this paper.)

where $\Delta G^r_{\text{fCO}_2,T_1}$ is the free energy of the given reaction calculated at pressure $P_1$ and temperature $T_1$. In the case of reaction (15) this is complicated by the necessity of taking into account the Boudouraud reaction ($\text{C} + \frac{1}{2}\text{O}_2 = \text{CO}$) so that thermodynamic expression for the dependence becomes:

$$f_{\text{fCO}_2} = \left[\chi_{\text{CO}} \cdot P_{\text{CO}}\right]^2 \cdot \exp\left(\frac{\Delta G^r_{\text{fCO}_2,T_1}}{R \cdot T_1}\right)$$

(17)

where $\chi_{\text{CO}}$ is the pure gas fugacity of CO at a partial pressure $P_{\text{CO}}$ (see EA-6). The values of $\Delta G^r_{\text{fCO}_2}$ for each of the reactions can be evaluated using the same procedure as that described for the siderite decomposition reaction (see EA-4). Using thermodynamic data from the most recent HP98 dataset and assuming a Peng–Robertson–Gasem cubic EOS for gas phase species the calculated univariant curves for reactions (11–15) at isobaric pressures of 1, 10 and 100 bars are shown in Fig. 7E.

From Fig. 7E the stability field for siderite can be viewed as a narrow wedge separating the hematite and magnetite stability fields that expands upward to lower $f_{\text{fCO}_2}$ values with increasing pressure. Under the range of temperatures and pressures considered (350–650 K and 1–100 bar) siderite is only thermodynamically stable at relatively low $f_{\text{fCO}_2}$ values\(^\text{14}\) with the upper section of the stability wedge defined by the interface between the siderite + gas = magnetite + gas fields corresponding to reaction (12). The upper and lower temperature limits for reaction (12) are bound by two invariant points in $T$ – $f_{\text{O}_2}$ space. The low temperature limit corresponds to the intersection of reactions (11, 12, and 14) at which point siderite is in equilibrium with both hematite and magnetite according to the equilibrium\(^\text{15}\):

$$\text{Fe}_2\text{O}_3 + 4\text{CO}_2 \rightleftharpoons 5\text{FeCO}_3 + \text{O}_2 \rightleftharpoons 2\text{FeCO}_3 + 6\text{CO}_2$$

(18)

While the higher temperature limit corresponds to the intersection of reactions (12, 13) and the graphite buffer reaction (15) at which point siderite is in equilibrium with magnetite and graphite according to the equilibrium\(^\text{16}\):

\(^\text{14}\) For reference $f_{\text{fCO}_2}$ values for the current atmospheres of Earth and Mars are $\sim 2 \times 10^{-1}$ and $1 \times 10^{-4}$ bar, respectively.

\(^\text{15}\) Applying the Gibbs phase rule we start with $\omega = \eta + r - 2$.

In the Fe–C–O, system we have three components plus an imaginary or inert gas (see footnote 14) so $\eta = 3 + 1 = 4$. There are three solid phases in equilibrium with a gas phase and so $\phi = 4$. The system has two independent chemical reactions (11) and (12) and so $r = 2$ (note reaction (14) is not independent since reaction (13) = $\frac{1}{2}$ reaction (11) – reaction (12)). Hence in $T$ – $f_{\text{O}_2}$ space $(r = 2)$ the variance is given by $\omega = 4 - 2 - 4 + 2 = 0$ again defining an invariant point.

\(^\text{16}\) Again applying the Gibbs phase rule $\omega = \eta + r - 1 - r$, we have three components for the Fe–C–O system plus an imaginary or inert gas so $\eta = 3 + 1 = 4$. There are three solid phases and one gas phase so $\omega = 4$, and we have two independent chemical reactions (12) and (13) so $r = 2$ (note reaction (15) is not independent since reaction (15) = $\frac{1}{2}$ (reaction (12) + reaction (13))). Hence in $T$ – $f_{\text{O}_2}$ space $(r = 2)$ the variance is given by $\omega = 4 - 2 - 4 + 2 = 0$ again defining an invariant point.
2Fe$_3$O$_4$ + 6CO$_2$ = 6FeCO$_3$ + O$_2$ = 2Fe$_2$O$_4$ + 6C + 6CO$_2$

(19)

Hence, it is therefore apparent that the partial decomposition of siderite to magnetite in the absence of graphite is only possible under an extremely limited set of $f_{O_2}$ conditions ($-44.46 < f_{O_2} < -44.30$ @ 1 bar; $-38.15 < f_{O_2} < -37.95$ @ 10 bar; and, $-31.95 < f_{O_2} < -31.67$ @ 100 bar).

4.2.2.5. Why is the residual carbonate composition so different? Table 1 of Treiman (2003) gives the composition of individual carbonate grains present in both the inner and outer magnetite-bearing layers. The average composition of these carbonate grains in the two layers therefore defines the residual carbonate composition that would have had to have been in equilibrium with magnetite during decomposition under thermodynamic control. Table 7 shows the average carbonate composition of both inner and outer magnetite layers based on data from Table 1 of Treiman (2003). This suggests that in the outer magnetite layer a residual carbonate with a 23 mol.% siderite component would have been stable with respect to further decomposition. Yet, the residual carbonate in the inner magnetite rim has a siderite component of ~29 mol.%, almost twice that of the outer rim. Such a carbonate would not have been thermodynamically stable under the temperature at which the outer carbonate would have been in equilibrium with magnetite. In the absence of any plausible mechanism to enable a large temperature gradient between the two layers, whose separation is only on the order of tens of microns, the sideritic composition of the residual carbonate in both layers should be very similar. The fact that they are not, makes any subsequent inferences based on the data provided in the Treiman (2003) Table 1 questionable. Treiman (2003) does suggest that the presence of other mineral phases in the carbonate grains analyzed could account for such inconsistencies, however no other investigation of ALH84001 carbonate has documented such phases at more than trace levels. This extreme difference in residual carbonate composition can be used to completely negate the Treiman (2003) equilibrium model for siderite decomposition.

4.2.2.6. Inferred volume abundances of magnetite in magnetite-bearing layers. Assuming all the magnetite present in the inner and outer magnetite rich rims are the products of partial thermal decomposition, and that these magnetites are essentially stoichiometric pure Fe$_2$O$_4$, then the initial composition of the carbonate prior to decomposition would have had a higher siderite content and a correspondingly lower magnebite content than the remaining residual carbonate. If we let the composition of the initial carbonate be Fe$_x$Mg$_{(1-x)}$CO$_3$, and the composition of the residual carbonate be Fe$_y$Mg$_{(1-y)}$CO$_3$, then the relevant chemical reaction is:

\[
\text{Fe}_x\text{Mg}_{(1-x)}\text{CO}_3 \rightarrow z \cdot \text{Fe}_x\text{Mg}_{(1-x)} + \beta \cdot \text{Fe}_2\text{O}_4 + 2\beta \cdot \text{CO}_2 + \beta \cdot \text{CO}
\]

(20)

where $z = \left(\frac{1-x}{1-x}\right)$ and $\beta = \frac{1}{2} \left(\frac{1-x}{1-x}\right)$. Several important observations can be immediately deduced:

- The number of moles of Fe and Mg in both the initial carbonate, and the carbonate-magnetite product are equivalent. Hence, the composition of the initial carbonate can be directly determined from the bulk composition of the carbonate-magnetite product.
- The number of moles and hence volumes of the residual carbonate and magnetite products are strictly bound by the mole fraction of Fe in the initial and residual carbonates (i.e., $x_0$ and $x_1$).
- The greater the proportion of magnetite product the smaller the mole fraction of Fe in the residual carbonate since $1 > x_0 > x_1 > 0$.

If we let $V_0$ and $V_1$ be the initial and residual volumes of carbonate, $V_2$ be the volume of magnetite, $V_3$ be the void space volume (since $V_0 > V_1 + V_2$) and $V_{FeCO_3}$, $V_{MgCO_3}$, and $V_{Fe_2O_4}$ are the molar volumes of siderite, magnesite and magnetite respectively (see Table 8) then from reaction (20) it is easy to show that:

\[
V_0 = x_0 \cdot V_{FeCO_3} + \left(1 - x_0\right) \cdot V_{MgCO_3},
\]

\[
V_1 = z \cdot \left(x_1 \cdot V_{FeCO_3} + \left(1 - x_1\right) \cdot V_{MgCO_3}\right),
\]

\[
V_2 = \frac{\beta}{2} \cdot V_{Fe_2O_4},
\]

\[
V_3 = V_0 - V_1 - V_2
\]

(21)

Table 8
Molar volumes of siderite, magnesite, and magnetite.

<table>
<thead>
<tr>
<th>Species</th>
<th>$V_m$ ($\times 10^{-3}$ m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCO$_3$</td>
<td>2.938</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>2.803</td>
</tr>
<tr>
<td>Fe$_2$O$_4$</td>
<td>4.452</td>
</tr>
</tbody>
</table>
From the Eq. (21) the fractional volume of magnetite, \( V_{\text{Fraction}}^{Fe_3O_4} \), in the final residual carbonate–magnetite assemblage is given by:

\[
V_{\text{Fraction}}^{Fe_3O_4} = \frac{V_2}{V_1 + V_2} = \frac{V_{Fe_3O_4} \cdot (x_0 - x_1) + 3 \cdot (1 - x_0) \cdot (x_1 \cdot V_{Fe_3O_4} + (1 - x_1) \cdot V_{MgCO_3})}{V_1 + V_2}
\]

Taking the inferred compositions of the initial and residual ALH84001 carbonate in the inner and outer rims from Tables 1 and 2 of Treiman (2003) we find that the fractional volume of magnetite inferred to be present in the outer rim to be only \( \sim 15\% \) and only \( \sim 43\% \) in the inner rim (Table 7). These values are inconsistent with any magnetite rim abundances reported in the literature, based on our observations, the volume fraction magnetite in these rims typically lies in the range of 50–70\%. This again suggests the observations, the volume fraction magnetite in these rims typically lies in the range of 50–70\%. This again suggests the hypothesis cannot explain the data in Treiman (2003).

4.3. Conflicting experimental observations

Two sets of direct experimental observations indicate a significant fraction of magnetites in ALH84001 carbonate arguably could not have formed by either the Brearley (2003) or Treiman (2003) models. These observations are:

- Magnetites embedded within the magnesite layer separating the inner and outer magnetite rich bands (e.g., Fig. 3G).
- Chemically impure magnetites with minor to trace amounts of Cr and/or Al (Fig. 5C).

In the first case, since the carbonate in the magnesite layer is essentially free of Fe, there is no siderite with which to decompose to form magnetite. In the second case since neither Cr nor Al can substitute into the trigonal \( R_3\text{c} \) structure of carbonate, thermal decomposition of carbonate alone cannot form magnetites with these elemental impurities. While we note that Treiman (2003) does allude to the presence of “smectite or Fe-oxyhydroxide adhering to the grains’ irregularities”, we have not observed any evidence of such surface coating in any TEM imaging of embedded magnetites. If such coating were the source of the observed Cr and/or Al then they would need to be relatively thick and would be obvious, even in casual observation.

4.4. Thermal decomposition studies of sideritic carbonates

Carbonate solid solutions between siderite and magnetite, rhodochrosite, and calcite can be viewed as the interpenetration, on an atomic scale, of two chemically different but structurally similar lattices (i.e., calcite; \( R_3\text{c} \)). For iron systems such as the carbonate minerals, the limits of solubility generally correlate with the relative size of the ions and their electrical charge in accordance with the Hume-Rothery rules (Hume-Rothery et al., 1969). Since the ions for octahedrally coordinated \( \text{Mg}^{2+} \), \( \text{Mn}^{2+} \), and \( \text{Fe}^{2+} \) are all similar (Table 9) they demonstrate complete solid solution series in essentially all geological environments. In the case of \( \text{Ca}^{2+} \), where the mismatch in radii is greater than \( \sim 10\% \), solid solutions within the calcite crystal structure are only possible over a relatively limited compositional range.

4.4.1. Prior studies

Thermal decomposition of mixed cation (\( \text{Mg, Ca, Mn} \))-siderites have been investigated under a wide variety of conditions, not only because of their geochemical importance, but also because they provide a convenient synthetic route to the preparation of complex metal oxides via the so-called ‘solid-solution-precursor’ method (Vidyasagar et al., 1984; Vidyasagar et al., 1985). The results of such studies are summarized in Table 6 and invariably demonstrate that thermal decomposition yields a mixed metal oxide phase as the product\(^7\). In general, substitution of \( \text{Fe}^{2+} \) by \( \text{Mg}^{2+} \) or \( \text{Mn}^{2+} \) in siderite increases its thermal stability (Dubrawski, 1991a; Dubrawski, 1991b), generally to a far greater extent than thermodynamic factors alone could account for. Furthermore, thermogravimetric analysis demonstrates that decomposition is accompanied by only a single endothermic peak (Dubrawski, 1991b) indicating the siderite component of the solid solution does not decompose independently.

4.4.2. Thermal decomposition of Roxbury siderite

Roxbury siderite represents a good terrestrial analog to the siderite-rich carbonate compositions suggested by Treiman (2003) to have decomposed to form the magnetite rich bands of the ALH84001 carbonates. Lane and Christensen

\( ^7 \) In this respect, it is worth re-emphasizing that not only do (\( \text{Mg, Mn} \))-siderites form a continuous substitutional solid solution series (magnesiowustite–manganowustite), but so do the intermediate (\( \text{Mg, Mn} \))–Fe-monoxides (magnesiowustite–manganowustite) and product (\( \text{Mg, Mn} \))–spinels (magnesiowustite–manganowustite).
reported here\textsuperscript{18}; both of which find that the thermal decomposition of a mixed cation siderite invariably results in the formation of mixed cation magnetite. We suggest, however, that the results obtained by Golden et al. (2006) are in fact entirely consistent with prior literature and the Roxbury siderite studies – it is only the interpretation of these results by Golden et al. (2006) that is flawed.

To illustrate this, it is first necessary to review the materials and methods used by Golden et al. (2006). The natural siderite used for their experiments was from Copper Lake, Antigonish County, Nova Scotia and is reported to have a bulk chemical composition of \((\text{Fe}_{0.643}\text{Mg}_{0.342}\text{Mn}_{0.012})\text{CO}_3\) (Golden et al., 2006). This siderite was partially decomposed in an evacuated sealed quartz tube by controlled heating, both in the presence of, and absence of, a natural pyrite containing minor silicate inclusions. The heating profile used was a slow temperature ramp (1 K \text{ min}^{-1}) from ambient up to 623 K for nine days before then cooling back again to ambient. Since the siderite only underwent partial decomposition to magnetite the residual carbonate was removed by dissolution in “20\% acetic acid followed by multiple washings with distilled \(\text{H}_2\text{O} \)”. The chemical composition of the remaining magnetite was then determined using TEM/EDX. In their results they report that Copper Lake siderite in the absence of pyrite produced magnetite containing only 7.1 mol.% Mg, while siderite in the presence of pyrite produced chemically pure magnetite (<1 mol.% Mg). At this point it is necessary to inject a few observations. It is clear that while the bulk composition of Copper Lake siderite may contain 34.5 mol.% Mg it cannot have been homogeneously distributed, since if it was there would be a single decomposition temperature associated with the siderite, and after nine days it would have either all decomposed or not decomposed at all. Though it could be argued that re-equilibration, by solid state cation diffusion, of Mg between magnetite product and unreacted carbonate could have lead to the thermal stabilization of the residual carbonate by increasing its Mg mole fraction, such cation diffusion at 623 K would not have been sufficiently facile to allow such a process (as discussed earlier). Fortunately, the issue of the compositional homogeneity of Copper Lake siderite was reported previously by Bell (2007), who is affiliated with the same research group as Golden et al. (2006) and so presumably used the same parent siderite sample.\textsuperscript{20} Fig. 7F taken from Fig. 3A, 3B-3G of Bell (2007) illustrates the variation of Mg and Fe abundances in a single grain surface ~175 × 175 \(\mu\)m of Copper Lake siderite. In this single region, there are at least three distinct carbonate compositions as illustrated in the histogram shown in Fig. 7F.

More importantly, one of these carbonate compositions is nearly pure siderite with only minor to trace Mg. Turning back to the decomposition experiments of Golden et al. (2006) it is clear that decomposition of Copper Lake

\textsuperscript{18} The use of high-power lasers with short wavelengths allows generation of the most extreme shock pressures in laboratories, but only in conjunction with extremely short pulse durations in the nanoseconds range. Laser irradiation shock experiments may be regarded as adequate simulations of hypervelocity impacts of microgram-mass micrometeorites onto atmosphere-free bodies such as the Moon as well as onto spacecraft\textsuperscript{17} from Langenhorst et al. (2002).

\textsuperscript{19} The “slow” heating studies of Roxbury siderite were conducted under essentially analogous conditions to those used by Golden et al. (2006).

\textsuperscript{20} This is consistent with the observation that both report identical compositions for their bulk Copper Lake siderite.
siderite will thus occur in a number of stages with increasing temperature, corresponding to the successive decomposition of progressively more Mg-rich carbonate components. At a temperature of 623 K only the stability field of the most Mg-poor siderite would have been crossed, resulting in the formation of a magnetite product that predictably has only a low Mg abundance. This is completely consistent with prior literature and the siderite decomposition studies reported here. That Golden et al. (2006) failed to fully characterize, or even take into consideration, the composition of their starting materials or determine the fraction of siderite that underwent decomposition or the fraction and composition of the residual carbonate, seem to invalidate any of their interpretations or conclusions.

4.5. Implications and origins of ALH84001 magnetites

The majority of ALH84001 magnetites are stoichiometrically pure Fe₃O₄ embedded within all compositions of carbonate ranging from the most Fe-rich (Fe₀.₆₀Mg₀.₁₆Ca₀.₀₅Mn₀.₀₅)CO₃) at the boundary of the inner and outer cores to the most Fe-free magnetite (Mg₀.₉₅Ca₀.₀₅)CO₃). It is difficult to suggest a process by which this magnetite has undergone thermal decomposition to produce chemically pure magnetite based on results from experiments in Table 6 and those of the Roxbury siderite decomposition studies reported here. Only a small fraction of Martian magnetite crystals are chemically impure; they contain trace to minor amounts of Cr (Fig. 5C) and/or Al (Thomas-Keprta et al., 2000a). Clearly these chemically impure magnetites have detrital origins and did not form as a consequence of thermal decomposition of host carbonate which lacks detectable Cr and/or Al.

Although the “thermal decomposition” hypothesis for the observation of chemically pure magnetites in the rims of ALH84001 carbonate disks appears, on the surface, to provide a simple inorganic explanation of the observations, theoretical and experimental evaluation indicates it is not applicable to the formation of the vast majority of the magnetites in ALH84001 carbonate disks (Table 10). As discussed at length previously, both the Brearley (2003) and Treiman (2003) hypotheses proposed to explain the presence of ALH84001 magnetite are flawed. The importance of experimental data therefore cannot be overestimated. We can summarize the experimental studies of decomposition of a mixed cation siderite with the following generalized reaction:

\[
3(\text{Fe}_{0.60}\text{Mg}_{0.16}\text{Ca}_{0.05}\text{Mn}_{0.05})\text{CO}_3 \xrightarrow{\Delta} (\text{Fe}_{0.60}\text{Mg}_{0.16}\text{Ca}_{0.05}\text{Mn}_{0.05})\text{O}_4 + 2\text{CO}_2 + \text{CO}
\]

While it is impossible to completely discount that some of the magnetites embedded in ALH84001 carbonates might be a product of thermal decomposition, we argue at best this can only account for a tiny portion. Consequently, this should not divert our attention from understanding the origin of the remaining majority of magnetites that would appear to have been derived from a detrital or allochthonous
Table 10
Features in ALH84001 consistent with carbonate decomposition.

<table>
<thead>
<tr>
<th>ALH84001 observations</th>
<th>Incompatibility with partial thermal carbonate decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micron scale isotopic and chemical heterogeneity present in carbonate disks, e.g., Valley et al. (1997), Saxton et al. (1998), Eiler et al. (2002), McKay et al. (1996) and this study</td>
<td>Increased cation diffusion at high temperatures would have erased chemical and isotopic gradients observed in the carbonate.</td>
</tr>
<tr>
<td>⁴⁰Ar/³⁹Ar chronometer in ALH84001 feldspathic glass last reset ~4 Ga (Weiss et al., 2002)</td>
<td>Heating above the Ar release temperature, ~350–500 °C, after 4 Ga would have reset ⁴⁰Ar/³⁹Ar chronometer.</td>
</tr>
<tr>
<td>Chemically pure magnetites present within all ALH84001 carbonate compositions including those contain no Fe (this study)</td>
<td>Breakdown temperature for thermal decomposition of Fe-containing carbonates to magnetite is a function of cation composition; the differing carbonate compositions in ALH84001 require different and incompatible temperature constraints. Magnetite cation composition reflects that of the carbonate from which it forms, i.e., chemically pure magnetite requires decomposition of chemically pure siderite. Magnetites present within the magnesite rim cannot have formed by magnetite decomposition since it contains no Fe.</td>
</tr>
</tbody>
</table>

A fraction of magnetites present in rim and core carbonate contain minor Cr and/or Al, e.g., Thomas-Keprta et al. (2000a) and this study.

Absence of graphite within carbonate disks, e.g., McKay et al. (1996), Flynn et al. (1998), Flynn et al. (1999), Clemett et al. (1998) and this study.

Some magnetites embedded within carbonate show evidence of surrounding void space, e.g., Barber and Scott (2002), Brearley (2003) and this study.

5. SUMMARY AND CONCLUSIONS

Two heating scenarios described herein provide the geological context for the decomposition models developed independently by Brearley (2003) and Treiman (2003). These models are contradictory; that is, they cannot both

Table 11
ALH84001 features in ALH84001 consistent with allochthonous magnetite.

<table>
<thead>
<tr>
<th>ALH84001 observations</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically pure magnetites embedded within a diverse range of carbonate compositions, including magnetite that contains no Fe (this study)</td>
<td>Embedding carbonate is not the progenitor of the magnetite – detrital magnetite incorporated during disk formation.</td>
</tr>
<tr>
<td>Fine-grained, S-containing, veins that cross-cut core carbonate (this study).</td>
<td>Influx of a sulfurous fluid(s) after carbonate disk formation.</td>
</tr>
<tr>
<td>Ferrihydrite embedded within fissures in the magnesite band (this study).</td>
<td>Influx of ferrous–ferric fluid(s) after carbonate disk formation.</td>
</tr>
<tr>
<td>Magnetites containing minor Cr and/or Al present in rim and core carbonate (Thomas-Keprta et al. (2000a) and this study).</td>
<td>Embedding carbonate is not the progenitor of the magnetite – detrital magnetite incorporated during disk formation.</td>
</tr>
<tr>
<td>Amorphous Si present in nanophase carbonate magnetite-rich rim and veins (this study).</td>
<td>Influx of siliceous fluid(s) either concurrent with or subsequent to rim/vein formation.</td>
</tr>
<tr>
<td>Spatially association of abundant Fe-sulfides with magnetite-rich rims but their relative scarcity within magnetite-rich veins (this study).</td>
<td>Influx of a sulfurous fluid(s) after carbonate disk formation.</td>
</tr>
<tr>
<td>Presence of void space associated with some magnetites embedded within both core carbonate and the magnesite band (Barber and Scott (2002), Brearley (2003), and this study). Presence of void space associated with some magnetites located at the interface of carbonate grains (this study).</td>
<td>Carbonate recrystallization enables migration of imperfections, such as magnetite and void spaces are to grain boundaries. (Conversely such spatial associations may simply be coincidental, e.g., void spaces are associated with magnetites in the magnesite band, but these magnetites could not have been produced by magnesite thermal decomposition.)</td>
</tr>
</tbody>
</table>
have occurred since application of one model negates the applicability of the other. The first is based on carbonate decomposition occurring under “extreme disequilibrium conditions” in which “kinetics are the dominant controlling factor” determining the chemical and physical nature of the magnetites that are formed. Although never explicitly addressed, this model is most consistent with the impact event that ejected ALH84001 from Mars. In the second model, carbonate decomposition occurs “at some depth beneath the Martian surface where the pressure was greater than the atmospheric pressure and the temperature declined slowly.” However, based on kinetic and thermodynamic arguments, both models proposed for the high temperature, inorganic formation of ALH84001 magnetite would not have produced the results observed in ALH84001 carbonate disks.

ALH84001 carbonate assemblages can be best explained as the result of low temperature, disequilibrium precipitation from a single fluid with variable composition or from multiple fluids. Nanophase magnetite and Fe-sulfides were suspended in fluids that formed the disk cores and rims. After deposition ALH84001 carbonate disks were exposed to multiple fluids containing amorphous silica, additional nanophase magnetite, and S- and Fe-rich phases, some of which were deposited in veins. While the majority of ALH84001 magnetites were deposited in silica enriched rims and veins, some are also distributed throughout the cores and within the magnetite bands. Most magnetites are chemically pure, although a few contain minor Al/Cr. Their presence is inconsistent with formation by thermal decomposition of their 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.

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