Signatures in magnetites formed by (Ca,Mg,Fe)CO₃ thermal decomposition: Terrestrial and extraterrestrial implications

Concepcion Jimenez-Lopez a,⇑, Carlos Rodriguez-Navarro b,⇑, Alejandro Rodriguez-Navarro b, Teresa Perez-Gonzalez a, Dennis A. Bazylnski c, Howard V. Lauer Jr. d, Christopher S. Romanek e

a Departamento de Microbiología, Facultad de Ciencias, Universidad de Granada, Campus de Fuentenueva s/n, 18071 Granada, Spain
b Departamento de Mineralogía y Petrología, Facultad de Ciencias, Universidad de Granada, Campus de Fuentenueva s/n, 18071 Granada, Spain
c School of Life Sciences, University of Nevada at Las Vegas, Las Vegas, NV, USA
d ESCG/Barrios Technologies, Houston, TX 77258, USA
e NASA Astrobiology Institute and Department of Earth and Environmental Sciences, University of Kentucky, Lexington, KY, USA

Received 29 June 2011; accepted in revised form 19 March 2012; available online 28 March 2012

Abstract

It has never been demonstrated whether magnetite synthesized through the heat-dependent decomposition of carbonate precursors retains the chemical and structural features of the carbonates. In this study, synthetic (Ca,Mg,Fe)CO₃ was thermally decomposed by heating from 25 to 700 °C under 1 atm CO₂, and by in situ exposure under vacuum to the electron beam of a transmission electron microscope. In both cases, the decomposition of the carbonate was topotactic and resulted in porous pseudomorphs composed of oriented aggregates of magnetite nanocrystals. Both calcium and magnesium were incorporated into nanophase magnetite, forming (Ca,Mg)-magnetites and (Ca,Mg)-ferrites when these elements were present in the parent material, thus preserving the chemical signature of the precursor. These results show that magnetites synthesized in this way acquire a chemical and structural inheritance from their carbonate precursor that indicates how they were produced. These results are not only important in the determination of the origin of chemically-impure, oriented nanophase magnetite crystals in general, but they also provide important insights into the origin of the large, euhedral, chemically-pure, [111]-elongated magnetites found within Ca-, Mg- and Fe-rich carbonates of the Martian meteorite ALH84001. Based on our experimental results, the chemically-pure magnetites within ALH84001 cannot be genetically related to the Ca-, Mg- and Fe-rich carbonate matrix within which they are embedded, and an alternative explanation for their occurrence is warranted.

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1. INTRODUCTION

Nanometer-sized magnetite (Fe₃O₄) crystals having a variety of morphologies, size distributions and chemical compositions have been recovered from modern and ancient environments (Thomas-Keprta et al., 2000). Magnetite is found on Earth in igneous, metamorphic and sedimentary rocks as well as in extraterrestrial materials including meteorites and interplanetary dust particles. Whereas magnetites formed at high temperature are clearly abiotic, those formed in low-temperature environments e.g., Precambrian stromatolites, deep-sea and lake sediments and soils, may have an abiogenic or biogenic origin (Thomas-Keprta et al., 2000). Biogenic magnetite is known to form...
through biologically-induced (BIM; Frankel and Bazyliński, 2003) or biologically-controlled mineralization (BCM; Bazyliński and Frankel, 2003). The origin of many low-temperature terrestrial magnetites is unknown, and there is still great controversy over how to distinguish inorganically- and biologically-produced sedimentary magnetites (Jimenez-Lopez et al., 2010). BCM magnetites have been proposed as magnetofossils by many authors because they simultaneously meet all the criteria summarized in the MAB package defined by Thomas-Keprta et al. (2000). BIM magnetites have not been generally accepted up to now as magnetofossils, with the exception of the extraordinary tabular single-domain magnetite crystals induced by Geobacter metallireducens GS-15 (Vali et al., 2004). The criteria contained in the MAB package, especially morphology, crystal-size and size distribution (i.e., Arató et al., 2005) have been widely used for many years to recognize biotic origin of natural terrestrial magnetites. However, many discussions have risen when trying to apply those criteria to extraterrestrial magnetites, and the debate still goes on (Thomas-Keprta et al., 2009). These problems must be resolved to recognize mineral biomarkers in terrestrial and extraterrestrial materials (Jimenez-Lopez et al., 2010).

In the laboratory, magnetite can be synthesized abiotically as a primary or secondary mineral phase. Secondary magnetite forms through the transformation of Fe-bearing minerals at low or high temperature. At low temperature (<100 °C), magnetite can be formed in solution by recrystallization of ferrihydrite, green rust and FeOOH under anoxic conditions (Ishikawa et al., 1998; Zachara et al., 2002). Alternatively, a solid-state transformation mechanism is proposed for the thermal decomposition of siderite (FeCO₃), or other Fe-rich carbonates, at higher temperatures in the absence of oxygen. Such a mechanism may be responsible for magnetite formation in natural environments resulting from the contact of a carbonate precursor with a magmatic fluid or from a meteoritic impact on sedimentary carbonates (Golden et al., 2001, 2004; Thomas-Keprta et al., 2009; Bell, 2007). The decomposition mechanism has been explored in some detail with distinct precursor minerals and under different environmental conditions (Golden et al., 2001, 2004; Thomas-Keprta et al., 2009), including thermal shock under conditions mimicking meteoritic impact (Bell, 2007). The thermal mechanism of magnetite formation has not been extensively explored with regard to the origin of terrestrial magnetites. Nevertheless, it has largely been debated in the context of the subset of magnetites with unusual chemical and physical properties that are intimately associated with carbonate disks in the ALH84001 Martian meteorite, related by some to a bacterial origin (McKay et al., 1996) and by others to an exclusively inorganic origin through the thermal decomposition of the carbonate matrix in which they are embedded (Golden et al., 2000, 2001, 2004; Brearley, 2003; Treiman, 2003; Bell, 2007). Golden et al. (2001) reported that magnetite crystals produced by the thermal decomposition of a mixture of pyrite, siderite, magnesite and ankerite were chemically-pure, single-domain and defect-free, similar to the [111]-elongated magnetite crystals observed in ALH84001. To bolster their results, Golden et al. (2006) thermally decomposed Copper Lake siderite in vacuo (closed system) whereas Bell (2007) decomposed this Copper Lake siderite by shocking samples to pressures up to 49 GPa. They obtained magnetites with compositions ranging from pure magnetite (when pyrite was present, (Golden et al., 2006)) to Mg-bearing magnetite (<10 wt%, (Golden et al., 2006) and ≤20 wt%, (Bell, 2007)) and claimed that these magnetites displayed the same range of sizes, compositions and morphologies as inorganic magnetites synthesized by Golden et al. (2004). Although a chemically diverse suite of magnetites were produced in these studies, no reaction products contained Ca. On the one hand, this is not surprising as Golden et al. (2006) did not report the presence of Ca in their starting material. On the other hand, Bell (2007) reported 11–14 wt% CaCO₃ in their siderite target, yet no Ca was observed in the solid phase product of the shock reaction. It is unclear why Ca was detected in the same starting material in one study but not the other but it is clear that a complex interaction of materials and processes influences the nature of solids produced by thermal decomposition.

Thomas-Keprta et al. (2009) challenged these results by thermally decomposing Roxbury siderite, which is considered to be a terrestrial analogue of the Fe-rich component of the carbonate disks in ALH84001 meteorite. They observed the formation of Mg- and Mn-magnetites and proposed that a CaCO₃ component separated from the (Ca,Mg,Fe)CO₃ solid solution prior to the formation of the magnetite. However, this phase, or CaO, was not observed in their experimental products.

To resolve discrepancies observed in these studies involving Ca incorporation in magnetites, and to shed light on signatures that may help recognize magnetite formation by the thermal decomposition of a carbonate matrix in natural environments, we studied the chemical composition and microtextural features of magnetites resulting from the decomposition (both thermally from 25 to 700 °C, and in situ, under the electron beam of a transmission electron microscope) of a synthetic (Ca,Mg,Fe)CO₃ (characterized in Romanek et al. (2009), Fig. 1). In particular, the fate of calcium in the resulting magnetite was monitored, and the structural relationship(s) between the precursor and product phases were determined.

2. METHODS

Synthetic mixed carbonate samples were provided by Romanek et al. (2009). They were precipitated in laboratory experiments conducted at 25 and 70 °C in free-drift experiments from solutions containing NaHCO₃, Fe(ClO₄)₂, Mg(ClO₄)₂ and Ca(ClO₄)₂. The resulting solids were identified by XRD as Mg and/or Ca-substituted siderites (samples FD15 and FD16) and Fe and/or Ca-substituted magnetites (samples FD20 and FD21). No magnetite was detected in these samples by XRD and/or TEM. The FD carbonates have a chemical composition (determined by inductively coupled plasma optical emission spectrometry; ICP-OES; Perkin-Elmer 4300DVS) listed in Table 1. A comparison of the chemistry of these synthetic carbonates with natural terrestrial and extraterrestrial (Ca,Mg,Fe)CO₃ is presented in Fig 1. Each sample was
separated into two aliquots: (1) a dry, powder sample and (2) sliced sections embedded in resin. In the latter case, samples were fixed with glutaraldehyde and post-fixed with osmium tetroxide. Afterwards, the sample was dehydrated with ethanol, and embedded in Embed 812. Ultrathin sections (50–70 nm) were prepared with a microtome (Reicher Ultracut S microtome, DIATOME diamond blade), mounted onto copper grids and carbon coated.

Both the dry powder sample and the sliced sections of (Ca,Mg,Fe)CO₃ were maintained in anaerobic conditions inside an anaerobic chamber (Coy Laboratory Products Inc.) and each decomposed to magnetite as described below.

2.1. Procedure 1

Mixed cation carbonates were decomposed by heating the dry, powder FD samples by differential scanning calorimetry (DSC). A sample was weighed in an alumina crucible to ±2 µg. The sample was then placed in the center of the hot zone of a small volume SENSYS evo DSC (Setaram Instrumentation; www.Setamat.com) differential scanning calorimeter. The instrument was sealed, evacuated and then flushed with pure CO₂ carrier gas for 10 min. The calorimeter was then purged with CO₂ at a rate of 5 cm³ min⁻¹. After CO₂ purged for 30 min, the sample temperature was ramped up to 700 °C at a rate of 20 °C min⁻¹. The sample was held at 700 °C for 10 min and then ramped down to room temperature. In a duplicate run, once the sample reached the maximum temperature (after 30 min), the process was repeated to ensure complete reaction and to obtain a curve for baseline subtraction. No microstructural, mineralogical or chemical differences were observed between magnetite crystals subjected to one or two heating events. Results reported here correspond to DSC-magnetites heated twice.

Sufficient material was produced in the reaction to determine the mineralogy of DSC-samples using a single-crystal X-ray diffraction equipped with an area detector (Bruker D8 SMART APEX, Germany). A frame (or 2-dimensional (2D) diffraction pattern) was collected under the following operating conditions: Mo Kα, 50 kV, 30 mA, 0.5 mm collimator diameter and 120 s exposure time. The XRD equipment used for the analyses has a CCD area detector that can register a 2D diffraction pattern containing complete Debye–Scherrer rings. These patterns were later integrated and converted into conventional 2theta scan for mineral identification. XRD2DScan software (Rodriguez-Navarro, 2006) was used to convert these 2D diffraction patterns into regular 20 linear scans. This software was also used for background subtraction and integration of peaks in the 20 scans. The integration of the intensity of rings allows better particle statistics even in very small samples (of a few µg) and the detection of individual mineral grains of minor phases. The detection limit for minor phases is generally established to be a few percent units (<5%) for conventional X-ray powder diffractometers but the detection limit of XRD equipment with area detector is much lower (Bhuvanesh and Reibenspies, 2003; He, 2009). In order to accurately determine the d-spacings for the main magnetite reflections, LaB₆ was used as an internal standard for angular calibration. The unit cell parameter (a) was determined using a line regression model: 

\[ d_{hkl} = \frac{a(h^2 + k^2 + l^2)^{0.5}}{2} \]

For this calculation, four of the strongest reflections of magnetite (e.g., 113, 004, 115 and 044) were considered.

The microstructure and composition of individual crystals was determined using a Philips model CM200 transmission electron microscope (TEM) (Philips, Eindhoven, The Netherlands: 200 kV, 10–20 µA, windows for analyses: 100 × 200 nm) equipped with an EDAX solid-state energy dispersive X-ray detector with an ultrathin window (UTW). For these analyses, DSC-magnetites were embedded in resin and sliced using the same protocol described above for the FD carbonate samples. At least 20 individual crystals were analyzed for each decomposed mixed cation carbonate sample. Quantitative analytical electron microscopy (AEM) and selected area electron diffraction (SAED) analyses were performed on the same spots of individual crystals on thin edges in scanning TEM (STEM) mode (<400 counts s⁻¹) using a 4 nm diameter beam, a 100 × 20 nm scanning area for AEM-TEM and a ca. 500 nm diameter circular area centered in the squared area for SAED. For AEM-TEM analyses, a low background condenser aperture and an analytical Be sample holder were employed to improve spectrum quality. Muscovite, albite, biotite, spersertine, olivine, and titanite standards were used to obtain k-factors (\( k_{a,i} / k_{a,D} \)), allowing X-ray intensities to be corrected for element analysis (Champness et al., 1982). The determined k-factor for Ca is 1.15, 1.35 for Fe and 1.07 for
Based on these k-factors, average errors for analyzed elements (two standard deviations), expressed as a percentage of the atomic proportions, are 5 (Mg), 3 (Ca), and 3 (Fe). Determination of the mineralogy of the crystals analyzed by AEM–TEM was performed by calculating d-spacings from SAED patterns, using the same analytical window. Measured d-spacings were compared to JCPD files from the International Center for Diffraction Data (ICDD) for mineral identification.

2.2. Procedure 2

Sliced sections of FD samples were decomposed in vacuo under the electron beam in a Philips model CM200TEM operating at 200 kV (Eindhoven, The Netherlands; 10–20 μA, beam spot size: 100 nm). Selected area electron diffraction (SAED) was performed to determine the zone axis of each crystal. Measured d-spacings were compared to JCPD files from the ICDD for both mineral identification and the determination of Miller Indexes of atomic planes parallel to the electron beam. The individual mixed cation carbonate crystal, held in the determined orientation, was then kept under the electron beam for 5–20 min to decompose it into magnetite. Decomposition was only achieved when using a large condenser aperture (200 μm). After phase transformation, SAED analysis was performed to determine the zone axis of the resulting product.

This procedure was performed on ~8 crystals from each mixed cation carbonate sample listed in Table 1 (with the exception of FD15). The resulting set of magnetite crystals are referred to as TEM-magnetites. The chemical composition of individual mixed cation carbonate precursors and the resulting TEM-magnetite crystals were analyzed by AEM–TEM, as described above for the DSC magnetites.

In the present study, low-substituted magnetites would be called (Ca,Mg)-magnetites while high-substituted magnetites would be addressed as (Ca,Mg)-ferrites, following the terminology in Orewczyk (1990) and Thomas-Keprta et al. (2009).

3. RESULTS AND DISCUSSION

3.1. Chemical signatures in magnetites formed by the decomposition of synthetic (Ca,Mg,Fe)CO₃

3.1.1. DSC-decomposition

Each mixed cation carbonate sample that was heated by DSC completely decomposed pseudomorphically into a porous aggregate of magnetite nanocrystals (Fig. 2) that retained the gross morphology of the precursor (Fig. 2c and d). None of the original carbonate matrix was detected by XRD in any case. Magnetite formed as a consequence of the decomposition of the precursor carbonate, in the absence of oxygen, but in the presence of CO₂. Note that the thermal decomposition of siderite in the absence of O₂ results in the formation of wüstite (FeO) and CO₂. CO₂ acts as an electron acceptor, thereby oxidizing the Fe²⁺ to Fe³⁺, during the reaction CO₂ → CO + 1/2O₂ (Gallagher and Warne, 1981). As a result, part of the Fe²⁺ in wüstite is
oxidized to Fe$^{3+}$, resulting in magnetite as the final solid phase (Gallagher and Warne, 1981; Brearley, 2003). Because of the molar volume differences between carbonate precursor and product oxide, a significant porosity (ca. 50%) was generated.

Non-isothermal DSC results displayed a maximum endothermal peak (representing carbonate decomposition) at 497 °C for DSC–FD15, 490 °C for DSC–FD16 (Fig. 2a), 577 °C for DSC–FD20 (Fig. 2b) and 560 °C for DSC–FD21 (Table 1). Because sample size/morphology, mass, and heating rate were similar for the different DSC–FD samples, variations in the decomposition temperature were mainly related to the carbonate composition, although other factors such as grain size and crystallinity may also account for slight changes in peak characteristics. The higher the Ca and Mg content (FD15 vs. FD20) the higher the decomposition temperature; conversely, the higher the Fe content (FD15 vs. FD20 and FD16 vs. FD21) the lower the decomposition temperature (Table 1). This is consistent with differences in decomposition temperature for the pure end-member minerals (Hurst et al., 1993; Brearley, 2003).

The size of DSC-magnetite crystals ranged from 5 to 40 nm and their morphologies ranged from hexagonal, to rectangular, rhombic and irregular (Fig. 2i and g). Well-developed chains of magnetite crystals were detected in all samples (Fig. 2g and e) with the exception of DSC–FD20. DSC-magnetites displayed a preferred crystallographic orientation with respect to each other, as revealed by both brightfield and darkfield TEM images (Fig. 2g; darkfield images not shown). Because the DSC–FD20 precursor was composed of an aggregate of randomly oriented submicrometer- to micrometer-sized carbonate crystals forming spherulites (Romanek et al., 2009), a preferred orientation (see the absence of Debye rings in SAED of Fig. 2h) occurred in small magnetite aggregates (ca. 200 nm in size; see squared section in Fig. 2h) corresponding to the individual crystals in the precursor. Bulk X-ray diffraction (XRD) analyses of the decomposed solids revealed the presence of magnetite for samples DSC–FD15 and DSC–FD21, and a mixture of magnetite and a small percentage of hematite for samples DSC–FD16 and DSC–FD20 (possibly due to partial oxidation of Fe$^{2+}$ during the analysis). No other minerals were detected by XRD (e.g., CaO, CaCO$_3$, and/or MgO minerals). Furthermore, systematic shifts in the d-spacings of magnetite reflections were detected, indicating that there is a modification of the unit cell dimensions due to the incorporation of Ca and/or Mg into the magnetite structure. The presence of Ca and Mg in magnetite was also confirmed by the detection of these cations by AEM–TEM in sliced sections of the magnetite crystals, as discussed below. In the case of sample DSC–FD16, XRD analyses reveal a significant contraction of the unit cell dimensions ($a = 8.253 \pm 0.005$ Å, compared to $a = 8.396$ Å for pure magnetite reported in the ICCD PDF 16-629). In sample DSC–FD20, there is only a slight contraction in the dimensions of the unit cell ($a = 8.347 \pm 0.005$ Å). In contrast, sample DSC–FD15 shows a significant expansion of the unit cell dimensions ($a = 8.495 \pm 0.005$ Å). The contraction or expansion of the unit cell is due, respectively, to the incorporation of smaller Mg$^{2+}$ (i.e., DSC–FD16) or larger Ca$^{2+}$ (i.e., DSC–FD15) ions into the magnetite structure, consistent with results of the AEM–TEM analyses. No evidence of oxidation of magnetite to maghemite ($\gamma$-Fe$_2$O$_3$) was detected by XRD.

Selected area electron diffraction (SAED) and analytical and transmission electron microscopy (AEM–TEM) were performed sequentially on the same selected areas while illuminating one or several nanocrystals of each DSC–FD sample. In all cases, SAED data yielded the typical d-spacings for magnetite, although these d-spacings were lower than those of magnetite in DSC–FD16, DSC–FD20 and DSC–FD21 samples and slightly larger than those of magnetite in DSC–FD15. These shifts could not be attributed to cation incorporation due to error associated with the SAED measurements. AEM–TEM analyses of the same selected area showed the presence of varying amounts of Ca and Mg in the magnetite nanocrystals, forming (Ca,Mg)–magnetites and (Ca,Mg)–ferrites. DSC–FD15 and DSC–FD20 crystals showed the presence of $\leq 6.8$ wt% (11 wt% in precursor) and 3 wt% (48 wt% in precursor) Mg, respectively, and the presence of $\leq 5.6$ wt% (26 wt% in precursor) and 13.2 wt% (23 wt% in precursor) Ca, respectively (Table 1). Analyses of individual crystals from DSC–FD16 and DSC–FD21 (no Ca in precursor) also showed the presence of $\leq 9$ wt% Mg (9 wt% in precursor) and 33 wt% Mg (64 wt% in precursor) Mg, respectively. Variability of Mg and Ca content between single crystals is attributed to chemical zoning in the precursor material, since these carbonates were grown in closed, free-drift experiments, in which the relative concentration of aqueous iron, calcium and magnesium varied throughout the time-course experiment (Romanek et al., 2009).

3.1.2. In situ TEM decomposition

After exposure to the electron beam for ~20 min in the TEM, each mixed carbonate crystal decomposed to a pseudomorph consisting of a porous aggregate of magnetite nanocrystals ~5–10 nm in size (Fig. 3). As for the DSC-samples, SAED and AEM–TEM analyses were performed sequentially on a specified area of individual crystals. SAED analyses yielded typical magnetite d-spacings. As observed in DSC magnetites, the calculated d-spacings were shifted to lower values in TEM–FD16, TEM–FD20 and TEM–FD21 and to higher values in TEM–FD15. AEM–TEM analyses of TEM–FD15 and TEM–FD20 crystals showed that they contained up to 4.3 and 33 wt% Mg, respectively, and up to 11.2 and 16.4 wt% Ca, respectively (Table 1), whereas TEM–FD16 and TEM–FD21 crystals (no Ca in precursor) contained up to 8.2 and 41 wt% Mg, respectively. As in the case of DSC magnetites, the variability of Mg and/or Ca within crystals of the same sample is correlated to the heterogeneous composition of the carbonate precursor. Although the Mg and/or Ca concentrations for some magnetites were close to the detection limit (±4 and 3 wt%, respectively), most of the crystals exhibited concentrations well above the detection limit.
Fig. 2. (a and b) DSC spectra of FD16 (a) and FD20 (b) samples. Both spectra show one endothermal peak, indicating the thermal decomposition of the carbonate; (c and d) TEM micrograph of mixed carbonate crystals from FD16 (c) and FD20 (d). Inset: AEM–TEM analysis showing the presence of Mg and Ca. (e and f) TEM images of product pseudomorphs showing porous aggregates of magnetite crystals that preserve the morphology of the precursor [DSC–FD16 (e) and DSC–FD20 (f)]. (g, h, i, and j) TEM images of DSC–FD16 (g and i) and DSC–FD20 (h and j) magnetite crystals. The arrows indicate magnetite crystals with facing corners. SAED patterns (d-spacing corresponding to magnetite) and AEM–TEM analyses (showing Mg and Ca) are included. AEM–TEM spectra: Mg is marked with a solid arrow and Ca is marked with a dotted arrow. Squares correspond to areas analyzed by AEM–TEM. SAED patterns correspond to a ca. 500 nm diameter circular area centered in the squared areas.
3.1.3. Chemical signatures observed in DSC- and TEM-magnetites

Considered collectively, XRD, SAED and AEM–TEM results show that the decomposition of the mixed carbonate results in the formation of (Ca,Mg)-substituted magnetite to (Ca,Mg)–ferrites as a solid solution, and not a mixture of separate phases (CaO + MgO + Fe3O4 or CaO + (Mg,Fe)3O4). Moreover, these data support the contention that spinodal decomposition of the substituted magnetites into pure end-members does not occur, nor does the re-carbonation of the oxides. The formation of a Mg-substituted magnetite (solid solution) from the thermal decomposition of Mg-substituted siderites is consistent with results reported by other researchers (Gallagher and Warne, 1981; Gallagher et al., 1981; Dubrawski, 1991; Gotor et al., 2000; Cohn, 2006; Isambert et al., 2006; Bell, 2007; Thomas-Keprta et al., 2009).

One of the most interesting results of this study is that Ca was incorporated in magnetite as a result of the carbonate mineral decomposition. These results are intriguing because Mg and/or Mn are known to co-precipitate in magnetite (ionic radius of 72 and 83 pm, respectively; Shannon, 1976), but the incorporation of Ca is more difficult because the ionic radius of Ca is relatively large compared to that of Fe2+ [ionic radius of 100 pm (Shannon, 1976) and 78 pm (Bloss, 2000), respectively]. Whereas the substitution of calcium in magnetite is not widely recognized in natural settings, it may occur through thermal decomposition mechanisms. Vidyasagar et al. (1984) demonstrated that a variety of complex metal oxides, including calcium ferrite (CaFe2O4) and brownmillerite (Ca2Fe2O5), can be produced by the thermal decomposition of CaCO3–FeCO3 solid solutions under air or oxygen at >400 °C. Calcium magnetite has been synthesized at high temperature from CaO– or calcite–hematite melts (Hryniewicz et al., 1971; Orewczyk and Jasienska, 1987; Orewczyk et al., 1995; Orewczyk, 2000), and low-temperature Ca–magnetite is documented in the remediation of acid mine drainage waters (Wang et al., 1996; Morgan et al., 2003).

In contrast, other researchers have not observed the incorporation of Ca in magnetite during the thermal decomposition of mixed-cation siderite (Gallagher and Warne, 1981; Gallagher et al., 1981; Ware and French, 1984; Dubrawski, 1991; Hurst et al., 1993; Isambert and Valet, 2003; Cohn, 2006; Isambert et al., 2006; Bell, 2007; Thomas-Keprta et al., 2009). Thomas-Keprta et al. (2009) suggest that the decomposition of an ankerite–dolomite solid solution would follow a sequential pathway in which the solid solution precursor separates first into calcite and a siderite–magnesite phase prior to the nucleation and growth of the magnetite. This proposed mechanism would yield either CaCO3 (or CaO) in the resulting products, but these phases were not observed in this study or those obtained by others (Gallagher and Warne, 1981; Dubrawski, 1991; Cohn, 2006; Isambert et al., 2006; Thomas-Keprta et al., 2009).

The failure to detect Ca in magnetite is most likely due to the low concentration of Ca in the precursor solids used in previous decomposition studies [maximum 1.3 wt% (Gallagher and Warne, 1981); trace amounts (Gallagher et al., 1981; Cohn, 2006); maximum 1.8 wt% (Isambert et al., 2006; shock pressures 8.4–25.9 GPa); 1.8 wt% (Thomas-Keprta et al., 2009)] compared to the present study (up to 25.5 wt% in FD15 and 22.8 wt% in FD20).

The effect of temperature on the chemistry of the resulting solid may also be critical. High temperatures could facilitate the spinodal separation of CaO from a Mg-magnetite (or Mg-ferrite) over time, as reported for the decomposition of double carbonates (Spinolo and...
Anselmi-Tamburini, 1989). Nevertheless, the results in the present study suggest that this process does not occur. Firstly, no CaO, calcite or other Ca-bearing mineral phase was detected by bulk XRD of the DSC-magnetites. Secondly, our results support the contention that the thermal history of the samples does not affect the chemical signature inherited from the precursor. In fact, TEM-magnetites (and/or ferrites) and DSC-magnetites (and/or ferrites) show the same chemical signatures, although they had different thermal histories [TEM-magnetites, analyzed directly after decomposition, were exposed to electron-beam heating (Egerton and Malac, 2004) at a T corresponding to the decomposition of siderite/impure-siderite in vacuum, i.e., \( \sim 385-450 \, ^\circ\text{C} \) (Brearley, 2003 and references therein), whereas DSC-magnetites were heated to 700 \(^\circ\text{C}\) (higher temperatures and time after decomposition compared to TEM-magnetites)]. Therefore, higher temperatures and/or longer heating times do not cause the spinoidal separation of the Ca and/or Mg-magnetites (and/or (Ca,Mg)-ferrites).

The main difference between these two sets of samples (TEM- and DSC-) is the crystal size (~5 nm for TEM-magnetites and ~40 nm for DSC-magnetites). These differences are caused by the coarsening of the oxide nanocrystals formed after decomposition [as previously reported for siderite (Angermann et al., 2010) and other carbonates (Rodriguez-Navarro et al., 2009)].

The formation of metastable solid solutions (rather than spinoidal separation), as a result of a thermal decomposition process, is also described for other double carbonates, such as dolomite (Spinolo and Anselmi-Tamburini, 1989) and impure siderite (Angermann et al., 2010). In fact, the thermal decomposition of double carbonates has been proposed as an efficient method for the low-T synthesis of (metastable) mixed metal oxides (e.g., (Mg,Ca)O (Spinolo and Anselmi-Tamburini, 1989) and (Mn,Zn,Fe)\(_3\)O\(_4\) (Angermann et al., 2010)). The resulting mixed oxides form via diffusionless, topotactic replacement of the parent carbonate (Spinolo and Anselmi-Tamburini, 1989), thus enabling the incorporation of metals cations of dissimilar radii in the oxide. According to the model proposed by Rodriguez-Navarro et al. (2009), the topotactic transformation occurs as a consequence of CO\(_2\) loss, accompanied by limited atom displacement, and shrinkage along specific \([hk0]\) directions in the transformed carbonate. During this process, new transient structures appear as well as empty spaces (vacancies) between cations (Rodriguez-Navarro et al., 2009). Calcium fills these spaces as the transient structure evolves in the inverse spinel oxide. Such metastable solid solutions persist over several hundred degrees above the decomposition temperature (Spinolo and Anselmi-Tamburini, 1989; Angermann et al., 2010). This explains why magnetites in the DSC and TEM experiments include Ca and/or Mg despite their different thermal history and the different relative concentration of cations in the precursor samples.

3.2. Topotaxy between the precursor (Ca,Mg,Fe)CO\(_3\) and the resulting magnetite

An additional experiment was performed with TEM–FD16, TEM–FD20 and TEM–FD21 to determine whether the transformation of the mixed carbonate to magnetite was topotactic (signifying a three-dimensional lattice continuity) between the reactant and product phases (Bloss, 2000). This study was performed to determine whether or not there was a genetic structural relationship between the precursor carbonate and the resulting magnetite to explain the pseudomorphic relationship between reactant and product observed in DSC-magnetites as well as the preferred crystallographic orientation among DSC-magnetites. Ultimately, this study provides a mechanistic model for the incorporation of Ca and/or Mg in magnetite.

Fig. 3a and b show mixed carbonate crystals (TEM–FD21) prior to decomposition by the electron beam. The SAED pattern shows that this crystal was a single phase, not a mixture of various carbonate phases. The crystal is oriented along the [010] zone axis (SAED in inset in Fig. 3b). After irradiation with the electron beam for 20 min, using a large condenser-lens aperture, a porous pseudomorph comprised of nanometer-sized magnetite crystals was produced (Fig. 3c). The pseudomorph had a typically mottled texture that is characteristic of beam-damaged carbonates (Wenk et al., 1983). The SAED pattern of the magnetite pseudomorph shows diffuse Debye rings where maxima are clearly observed, indicating that the magnetite nanocrystals display a highly oriented arrangement, consistent with the bright field image of the pseudomorph presented in Fig. 3c. In fact, the SAED in Fig. 3c shows that the [110] zone axis of magnetite crystals is parallel to the [010] zone axis of the precursor carbonate (Fig. 3b). A second systematic orientation relationship is the \([441]_{\text{carb}}//[110]_{\text{mag}}\). It follows that two of the periodic bond chains (PBC) of the carbonate precursor (i.e., those parallel to \([441]\) and \([010]\) directions) transform into the \(<110>\) direction in the oxide product. These topotactic orientation relationships, observed in all samples studied (see also Fig. 4), are identical to those found in other carbonate such as calcite, whose thermal decomposition is also topotactic (Rodriguez-Navarro et al., 2009). Interestingly, other researchers such as Thomas-Kep graphical patterns of magnetite nanocrystals produced during thermal decomposition of Fe-rich carbonates with similar features as those presented here, demonstrating a preferred orientation of the magnetite crystals (see Fig. 6b in Thomas-Kep (2009) and Fig. 9 in Bell (2007)). Nevertheless, these authors do not comment on the fact that their observations indicate a topotactic decomposition of the precursor carbonate.

Rodriguez-Navarro et al. (2009) reported that oxide nanocrystals (about 5 nm in size), formed during the early stages of \textit{in situ} carbonate (calcite) decomposition in the TEM, aggregated in an oriented fashion following the collapse of the mesoporous structure, similar to that shown in Fig. 3c. This transformation is associated with a release of mechanical stress from the mismatch between the structure of the reactant and product phase during the topotactic decomposition. After this diffusionless coarsening process, sintering associated with increased temperature and heating time contributes to the final growth of the crystals to produce the grain sizes observed in DSC experiments when heating continues above the decomposition temperature.
of carbonates (Rodriguez-Navarro et al., 2009; Angermann et al., 2010). Most important, the coarsening process does not modify the crystallographic relationship between parent and product phases, nor the chemical signature (i.e., Ca and/or Mg incorporation), thus preserving the original topotactic relationship and the chemical fingerprint under temperature conditions spanning from very low-\( T \) (~382–450 °C, TEM) up to high-\( T \) (700 °C, DSC). In fact, thermally-activated decomposition of carbonates such as dolomite, ankerite, siderite, magnesite, ottavite, smithsonite,
cerusite, and calcite (Rodriguez-Navarro et al., 2009 and references herein) has been shown to be topotactic and not dependent on heating rate, peak $T$ or heating time, and $pCO_2$ (Rodriguez-Navarro et al., 2009). Thus, a similar crystallographic relationship is expected between reactant/product regardless of the thermal history of the sample.

3.3. Implications for terrestrial and extraterrestrial magnetites

The experiments from the present study demonstrate that magnetite produced by the thermal decomposition of (Fe,Mg,Ca)CO$_3$ preserves a legacy of the geochemistry and structural attributes of the phase from which it formed. These signatures could be important in recognizing the origin of some terrestrial and extraterrestrial nanomagnetites formed through this inorganic pathway. In this context, the chemical and structural signatures observed in this study could provide insights, for example, in recognizing the origin of nanophase (Mg,Ca)-magnetites, that may result from the thermal decomposition of (Fe,Mg,Ca)CO$_3$ under a CO$_2$ rich atmosphere [as likely existed on Early Earth (Ohmoto et al., 2004) and possibly on Early Mars], following events such as meteoritic impacts or metasomatism.

In the case of magnetites of the ALH84001 Martian meteorite, our results suggest that aggregates of anhedral, fine-grained magnetites observed by Barber and Scott (2003), typically near fracture zones, are consistent with the partial decomposition of ALH84001 carbonates, since these authors show a crystallographic orientation with the surrounding carbonate similar to that observed in the present study. This thermal decomposition probably occurred at a temperature not intense enough to fully decompose the carbonate and to coarsen the magnetites to produce larger euhedral crystals. On the other hand, the textural and chemical analyses presented in this study show that chemically pure, euhedral magnetite crystals ranging in size between 30 and 50 nm in ALH84001 carbonate disks are not consistent with a thermal decomposition event. It is important to note that the chemical purity of these magnetites is still being debated. Some authors claim that they contain up to 3% Mg (Golden et al., 2006; Bell, 2007) while others defend the chemical purity of these magnetites (Thomas-Keprta et al., 2000). Nevertheless, and in the context of structural relationships, Barber and Scott (2002) concluded that there was topotaxy between euhedral magnetite nanocrystals and Ca,Mg,Fe-carbonates in ALH84001. Note, however, that their conclusions were based on the orientation relationship defined by McTigue and Wenk (1985) in calcite. The latter have been recently reinterpreted by Rodriguez-Navarro et al. (2009) as follows: during a thermal decomposition event, and upon the devolatilization of CO$_2$, the CO$_2^-$ groups in the PBC directions of siderite (Fig. 5a) convert to O$_2^-$ groups, which subsequently rearrange along with metal cations along the [110] direction for the product oxide (Fig. 5b). In other words, magnetites align along the [110] directions, which are parallel to the original PBC direction of the carbonate precursor (Fig. 5c and d). Such an orientation relationship between the carbonate precursor and the chemically-pure, surrounding carbonate similar to that observed in the present study. This thermal decomposition probably occurred at a temperature not intense enough to fully decompose the carbonate and to coarsen the magnetites to produce larger euhedral crystals. On the other hand, the textural and chemical analyses presented in this study show that chemically pure, euhedral magnetite crystals ranging in size between 30 and 50 nm in ALH84001 carbonate disks are not consistent with a thermal decomposition event. It is important to note that the chemical purity of these magnetites is still being debated. 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In other words, magnetites align along the [110] directions, which are parallel to the original PBC direction of the carbonate precursor (Fig. 5c and d). Such an orientation relationship between the carbonate precursor and the chemically-pure,

![Fig. 5. Orientational relationships between siderite and magnetite structures. (a) structure (left) of the hexagonal unit cell of siderite, R3c space group, showing the stacking of alternate layers of Fe$^{2+}$ and CO$_2^-$ ions along the c-axis. The projection of the structure on the (10 14) rhombohedral cleavage plane (right) shows the different PBCs (Periodic Bond Chains) existing in this carbonate; (b) the structure of magnetite, Fd3 m space group, showing the orientation of the [110] and [111] directions; (c) structural/orientational relationships between the carbonate (10 14) planes, and PBC directions, and the magnetite crystals formed upon thermal decomposition of the carbonate precursor, with <441>carbonate // [110]magnetite and [010]carbonate // [110]magnetite; (d) example of magnetite crystals aligned // to [110]magnetite formed upon thermal decomposition of the siderite precursor in the DSC and observed in the TEM.](image-url)
they are embedded, supporting the conclusions of phase lead to the conclusion that large, chemically-pure, produced through thermal decomposition of a precursor magnesite, but none in association with ferro-

associated with nanopores and in contact with partially the carbonate matrix in which they are embedded, and an could not be produced by the thermal decomposition of alternative mechanism for their formation must be sought.

ments that greatly improved this manuscript.

We also thank A. Mucci and H. Vali for valuable com-

to Johnson Space Center (NASA) for the DSC analyses, and to EAR-0920718 and A.R.N. by Grant CTM2007-65713. Thanks go to Johnson Space Center (NASA) for the DSC analyses, and to the CIC personal from the University of Granada for technical assistance. We also thank A. Mucci and H. Vali for valuable comments that greatly improved this manuscript.

ACKNOWLEDGEMENTS

Financial funding was provided by Grants CGL2007-63859, CGL2010-18274 and MAT2009-11332 from the Spanish Ministry of Science and Innovation (MCI) and GREIB (BIO103) from Junta de Andalucia. This research was also funded in part by a Grant to C.S.R. through the NASA Astrobiology Institute. D.A.B. is supported by US National Science Foundation Grant EAR-0920718 and A.R.N. by Grant CTM2007-65713. Thanks go to Johnson Space Center (NASA) for the DSC analyses, and to the CIC personal from the University of Granada for technical assistance. We also thank A. Mucci and H. Vali for valuable comments that greatly improved this manuscript.

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**Associate editor:** Alfonso Mucci