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Thermal history of ALH 84001 meteorite by Fe^{2+}-Mg ordering in orthopyroxene

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Abstract–A single orthopyroxene crystal from the Martian meteorite Allan Hills (ALH) 84001 was studied by X-ray diffraction (XRD) and electron microprobe analysis (EMPA) to retrieve information about its thermal history. Both sets of data were used to measure the Fe^{2+}-Mg order degree between the M1 and M2 sites expressed by the distribution coefficient k_D. The 529 ± 30 °C closure temperature (T_c) of the Fe^{2+}-Mg ordering process of ALH 84001 orthopyroxene (Fs_{28}) was calculated using Stimpfl (2005a, 2005b) $\ln k_D$ versus $1/T$ equation obtained for intermediate iron sample. At this T_c, the orthopyroxene cooling rate, calculated by Ganguly's (1982) numerical method, was 0.1 °C/day. This study puts new constraints on the last high-temperature thermal episode recorded by orthopyroxene. With reference to the geological history (Treiman 1998), we ascribe this episode to the I3 event, and we interpret the T_c of 529 °C as a lower limit for this impact heating. Our data confirm that experimentally defined physical conditions for the formation of magnetite from decomposition of carbonates took place on the Martian surface during event I3.

INTRODUCTION

Allan Hills (ALH) 84001 is a coarse-grained Martian orthopyroxenite formed in a plutonic environment. This meteorite has received enormous attention since some of its features were interpreted as evidence for ancient biogenic activity on the red planet (McKay et al. 1996; Gibson et al. 2001). In an examination of evidence regarded by several researchers as proof of biological activity, Treiman (2003) proposed a new comprehensive hypothesis in which geological processes can account for the purported biogenic features, with no need for biological mediation.

In this hypothesis, the formation of submicron magnetite crystals from the decomposition of previously deposited iron-rich carbonates is triggered by the thermal overprint generated by the impact shock event (I3) (Treiman 1998, 2003). According to Treiman (2003), this impact event heated ALH 84001 rock to a temperature of 227–427 °C (or locally higher). Cooling after the peak temperature is less constrained, but it was expected by Treiman (2003) to be relatively slow, allowing the magnetite crystal to reach chemical equilibria with surrounding minerals and gas.

New constraints on the thermal history of this rock can be established by estimating the Fe^{2+}-Mg order degree in the ALH 84001 orthopyroxene. Intracrystalline Fe^{2+}-Mg exchange reaction between the octahedral sites in this mineral is a reversible process that is orders of magnitude faster than intercrystalline Fe^{2+}-Mg diffusion. This reaction is thus able to record the latest event in the thermal evolution of the host rock. Once the thermodynamics and kinetics of the Fe^{2+}-Mg exchange process are known, orthopyroxene can be used to retrieve the thermal history of its host rocks. Empirical equations expressing the equilibrium distribution coefficient k_D as a function of temperature were obtained by isothermal annealing to equilibrium of orthopyroxene samples with different composition in fO_2-controlled conditions (Saxena and Ghose 1971; Molin et al. 1991; Yang and Ghose 1994; Stimpfl et al. 1999; Schlenz et al. 2001; Stimpfl 2005b). These calibrations allow the estimation of closure temperature (T_c) for the Fe^{2+}-Mg exchange in an orthopyroxene crystal from its quenched ordering state.

A quantitative estimate of cooling rates can be retrieved from the quenched ordering state of the orthopyroxene following the procedure developed by Ganguly (1982) in accordance with Mueller's model (1967, 1969). This method

Table 1. Unit cell parameters and information on data collection and structure refinement.

	OPX ALH 84001 N.1
Dimension (mm) of the crystal	0.05 × 0.150 × 0.180
a (Å)	18.2987(17)
b (Å)	8.8759(8)
c (Å)	5.2136(5)
V (Å^3)	846.78(5)
$I_{\mathrm{ind.}}$	1589
R_{int} (%)	3.90
R_{all} (%)	6.02
R_{w} (%)	12.77
S	1.222
m.a.n. M1	13.12(5)
m.a.n. M2	19.29(6)
m.a.n. (M1 + M2)	32.41
<M1-O> (Å)	2.085(3)
<M2-O> (Å)	2.195(3)

Note: standard deviations are given in parentheses. I_{ind} is the number of independent reflections used for structure refinement; $R_{int} = \Sigma\left|F_o^2 - F_o^2(\mathrm{mean})\right| / \Sigma[F_o^2]$ where F_o and F_c are the observed and calculated structure factors; $R_{all} = \Sigma\left|\left|F_o^2\right| - \left|F_c^2\right|\right| / \Sigma[F_o^2]$; $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{0.5}$, where n is the number of reflections and p is the total number of parameters refined; m.a.n. is the mean atomic number (in electrons per formula unit) before introducing the chemical constraints.

is based on the calculation of the rate constant (K$^+$) for the Fe^{2+}-Mg exchange reaction as a function of temperature and composition. This calculation has been performed by several researchers (Virgo and Hafner 1969; Besancon 1981; Anovitz et al. 1988; Saxena et al. 1987, 1989; Skogby 1992; Sykes-Nord and Molin 1993; Ganguly and Tazzoli 1994; Zema et al. 1999; Heinemann et al. 2000; Zema et al. 2003; Stimpfl et al. 2005) thus allowing the orthopyroxene to be used as a "geospeedometer" for retrieving the thermal history of its host rock. This method has already been applied to several terrestrial and extraterrestrial rocks (Ganguly 1982; Ganguly et al. 1994; Molin et al. 1994; Ganguly and Domeneghetti 1996; Kroll et al. 1997; Zema et al. 1997; Domeneghetti et al. 2000; Ganguly and Stimpfl 2000; Stimpfl et al. 2005; McCallum et al. 2006), but has never been used for the ALH 84001 meteorite. The aim of this work is to apply the orthopyroxene geospeedometer to ALH 84001 sample by measuring the Fe^{2+}-Mg ordering state through single-crystal X-ray diffraction (XRD). Preliminary results were presented by Domeneghetti et al. (2006a).

EXPERIMENTAL

Sample

A small fragment (0.14 g) of ALH 84001,376 orthopyroxenite was obtained from the meteorite sample curator at NASA Johnson Space Center. Orthopyroxene grains in the ALH 84001 meteorite are crushed and deformed due to shock; careful selection of single crystals under the polarizing microscope was necessary. Only one single crystal (0.050 × 0.150 × 0.180 mm) showing sharp extinction was found to be suitable for X-ray data collection, though it exhibited wide diffraction profiles. The same crystal was analyzed by electron microprobe after the diffraction work was done.

X-Ray Single-Crystal Diffraction and Structure Refinement

Intensity data were collected on a three-circle Bruker AXS SMART APEX diffractometer, equipped with a CCD detector (graphite-monochromatized MoKα radiation, λ = 0.71073 Å, 55 kV, 30 mA) and a monocap collimator. The Bruker SMART software package was used. A total of 3600 frames (frame resolution 512 × 512 pixels) were collected with six different goniometer settings using the ω-scan mode (scan width: 0.3°ω; exposure time: 15 s·frame^{-1}; detector sample distance: 6.02 cm). About 15,639 reflections were collected. Completeness of the measured data was achieved up to 30°θ. The Bruker SAINT+ software was used for data reduction, including intensity integration and background and Lorentz-polarization corrections. Due to the high mosaicity shown by the crystal, box optimization was allowed during the integration. The semi-empirical absorption correction of Blessing (1995), based on the determination of transmission factors for equivalent reflections, was applied using the program SADABS (Sheldrick 1996) and the monoclinic Laue group 2/*m*. The unit-cell parameters, obtained by a least-squares procedure that refines the position of about 900 reflections in the range 12–22°θ are reported in Table 1. The same table also reports the value of discrepancy factor R_{int}, calculated on the average of $[F_o]^2$ values of equivalent pairs in Laue symmetry. The presence of some very weak (*0kl*) "forbidden reflections" with $k = 2n + 1$ and $l = 4n + 2$, which is consistent with reflections from *C*2/*c* clinopyroxene exsolved on (100) and superimposed on the (*0kl*) "forbidden reflections" of the orthopyroxene was noted. The structure refinement was then carried out following the procedure of Domeneghetti et al. (1996) for a *Pbca* phase coexisting with a *C*2/*c* exsolved. The fraction of exsolved *C*2/*c* phase was calculated to be 0.44(10)% and was thus negligible, which is in agreement with Berkley and Boynton (1992), Mittlefehld (1994), and Treiman (1995), who did not observe pyroxene exsolution lamellae in this sample. The observed F_o^2 values were then treated with a full-matrix least-squares refinement in *Pbca* space group by SHELX-97 (Sheldrick 1998), using individual weights and the weighting scheme suggested by the program. No threshold or cutting of low-intensity reflections was applied, following the recommendations of Merli et al. (2002) suggested by the leverage analysis applied to the orthopyroxene. The atomic scattering curves were taken from *International tables for X-ray crystallography*

(Ibers and Hamilton 1974). Neutral versus ionized scattering factors were refined in all sites that are not involved in chemical substitutions (Hawthorne et al. 1995); complete ionization for Mg and Fe in M1 and M2 sites was assumed. The extinction correction was applied with the procedures of program SHELX-97. Table 1 also reports the mean atomic numbers (m. a. n.) in electrons per formula unit (epfu) at the M1 and M2 sites obtained when the structure refinement reached convergence before introducing the chemical constraints.

Electron Microprobe Analysis

After XRD study, the crystal was embedded in epoxy resin and polished for electron microprobe analysis. A Cameca-Camebax electron microprobe with a fine-focused beam (1 µm in diameter) operating in the wavelength-dispersive (WDS) mode was used. Operating conditions were 15 kV accelerating voltage and 15 nA beam current; counting times were 20 s at the peak and 20 s at the background. The following synthetic end-member mineral standards were used: diopside for Mg, ferrosilite for Fe, wollastonite for Si and Ca, chromite for Cr, corundum for Al, $MnTiO_3$ for Mn, and Ti, a natural albite (Amelia albite), for Na. X-ray counts were converted into oxide weight percentages using the PAP correction program. Analyses are precise to within 1% for major elements and 3–5% for minor elements. The results of the chemical analysis are reported in Table 2. The crystal chemical formula was calculated on the basis of six oxygen atoms, following Papike (1969). Fe^{3+} was calculated by stoichiometry following Droop (1987). When all elements are accurately measured, calculated Fe^{3+} provides a reliable indication of the $Fe^{3+}/\Sigma Fe$ in pyroxene (Domeneghetti et al. 2006b). The absence of Fe^{3+} in ALH 84001 pyroxene, as inferred from electron microprobe data, is in perfect agreement with data reported in Delaney and Dyar (2000). Only those spot analyses with total cation contents of 4.000 ± 0.005 atoms on the basis of six oxygen atoms and charge balance $3^{[4]}Al + Na - 3^{[6]}Al - 4Ti - 3Cr \le |0.005|$ were selected and averaged. These data agree with those provided by Mittlefehldt (1994). Table 2 also reports the sum of the m.a.n. at M1 and M2 sites (32.43 epfu) calculated from the analysis. This value is in very good agreement with the sum of the m.a.n.s of M1 and M2 sites obtained from the structure refinement before introducing chemical constraints (32.41 epfu).

Determination of the Fe^{2+}-Mg Ordering State

Full-matrix least-squares with chemical constraints, taken from the chemical analysis and assuming 1σ error, were carried out to obtain the site partitioning. M1 and M2 site distribution was obtained by considering Mn fully ordered in the M2 site in accordance with the stronger preference for the M2 site of Mn compared to Fe^{2+} observed by Stimpfl (2005a, 2005b) in a donpeacorite sample. The following restraints were also introduced into the refinement:

1. All structural sites were considered fully occupied.
2. Al was distributed between the TB and M1 sites.
3. Fe^{3+}, Cr^{3+} and Ti^{4+} were considered fully ordered at the M1 site.
4. Mg and Fe^{2+} were allowed to fractionate between the M1 and M2 sites.
5. Ca and Na were assumed to occupy M2 site.
6. The charge balance in the isomorphous replacements was ensured by the equation.

Table 2. Electron microprobe analysis and formula in atoms per formula unit (apfu) based on six oxygen atoms.

OPX ALH 84001 N.1 (averaged spots 9)			
% oxides		a.p.f.u	
SiO_2	54.82(23)	Si	1.9782(39)
TiO_2	0.16(2)	Ti	0.0043(6)
Al_2O_3	0.67(3)	Al	0.0283(14)
Cr_2O_3	0.40(8)	Cr	0.0113(22)
FeO	17.77(23)	Fe^{2+}	0.5363(53)
MnO	0.51(3)	Mn	0.0155(9)
MgO	25.18(12)	Mg	1.3545(38)
CaO	1.78(7)	Ca	0.0688(27)
Na_2O	0.02(2)	Na	0.0013(15)
Total	101.29(37)	Total	3.998(30)
		m.a.n.[a]	32.43(12)

[a] Calculated total mean atomic number for M1 and M2 sites, in electrons per formula unit.

The discrepancy indices R_{all} and R_w based on all the F_o^2, the goodness of fit (*S*) and the observed mean bond distances for the M1 and M2 sites (<M1-O> and <M2-O>) are reported in Table 1. The site populations are reported in Table 3; the positional and atomic displacement parameters are reported in Table 4. Table 5 (available from the authors) lists the observed and calculated structure factors.

The Fe^{2+}-Mg ordering state was estimated using the intracrystalline distribution coefficient k_D expressed as:

$$k_D = X_{Fe}^{M1}(1 - X_{Fe}^{M2}) / X_{Fe}^{M2}(1 - X_{Fe}^{M1}) \qquad (1)$$

where $X_{Fe}^{M1} = (Fe)_{M1}/(Fe + Mg)_{M1}$ and $X_{Fe}^{M2} = (Fe)_{M2}/(Fe + Mg)_{M2}$. The k_D value 0.0685(29) is reported in Table 3.

RESULTS AND DISCUSSION

Because we found only one orthopyroxene crystal in this meteorite sample suitable for XRD analysis, we could not perform isothermal annealing experiments at various *T* until equilibrium to obtain an experimental calibration $\ln k_D$ versus $1/T$. The closure temperature for ALH 84001 orthopyroxene (Fs_{28}, $\ln k_D = 0.0685$) was then calculated by using the calibration curve determined by Stimpfl (2005a, 2005b) for the HO sample (Fs_{50}) as follows:

Table 3. Site populations.

Opx ALH 84001 n.1		
T	Si	1.9777
	Al	0.0223
M1	Mg	0.9130(26)
	Fe	0.0668(28)
	Fe^{3+}	0.0000
	Al	0.0060
	Cr	0.0101
	Ti	0.0041
M2	Mg	0.4416(27)
	Fe	0.4715(33)
	Ca	0.0693
	Mn	0.0156
	Na	0.0020
	X_{Fe}^{M1}	0.0682
	X_{Fe}^{M2}	0.5164
	k_D	0.0685(29)

Note: $K_D = X_{Fe}^{M1}(1 - X_{Fe}^{M2}) / X_{Fe}^{M2} - (1 - X_{Fe}^{M1})$.
The site occupancy values represent atoms per six oxygen.

$$\ln k_D(\text{Fe-Mg}) = -2708(\pm 58)(T + 0.695(\pm 0.058) \quad (2)$$

which yields T_c = 529(±30) °C. This procedure appears to be reasonable because:

- There is no significant dependence of k_D on iron content in the range Fs_{19}–Fs_{75} (Stimpfl et al. 1999) when the compositions of orthopyroxene are close to the Fe-Mg binary.
- The compositional differences in minor elements between our sample and the above quoted HO (Δ_{Al} = 0.017; Δ_{Mn} = 0.002; Δ_{Cr} = 0.011 a.p.f.u.) are negligible.
- As to differences in Ca content (Δ_{Ca}= 0.031 a.p.f.u.), annealing experiments carried out by Zema et al. (1999) on the Ca-rich orthopyroxene from the Johnstown diogenite [Ca= 0.054(3) a.p.f.u.] showed that the Fe-Mg equilibrium behavior is not affected by the presence of this element. Furthermore, kinetic data obtained by Zema et al. (2003) in annealing experiments carried out on an even more Ca-rich orthopyroxene (Ca = 0.088[3] a.p.f.u.) are in perfect agreement with those expected for a normal kinetic behavior for the Fe^{2+}-Mg exchange reaction.

We modelled the cooling rate using an asymptotic cooling law: $1/T(K) = 1/T_o + \eta t$ where T_o is the initial temperature and η is the cooling time constant (Ganguly 1982). The calculation of η was carried out using the program CRATE (Ganguly, personal communication) in which the continuous cooling process of the sample is simulated by a series of isothermal steps. To calculate the Fe/Mg order degree reached at each step we used both the equilibrium k_D obtained at the corresponding temperature from Equation 2, as well as the kinetic constant calculated for that temperature by the following equation:

$$\ln(C_o K^+) = (28.26 + 5.27X_{Fe}) - (41,511 - 12,600X_{Fe})/T(K), \text{min}^{-1} \quad (3)$$

This Arrhenian expression, which takes into account the dependence of C_oK^+ on temperature and on X_{Fe}, was obtained by Stimpfl et al. (2005), who performed kinetic experiments on orthopyroxene samples of different composition using the WI buffer. However, for this calculation, we assumed that the fO_2 conditions on Mars correspond to those controlled by a QMF buffer (calculated at 1 bar) and that the disordering rate constant increases with $(fO_2)^{-1/6}$. Our basis for this was the experiments carried out by Stimpfl et al. (2005), which demonstrated that the rate constant in orthopyroxene varies as $fO_2^{1/n}$ with n = 5.5–6.5. Changing fO_2 from the value of ~10^{-32} bar defined by WI buffer to ~10^{-24} defined by QMF buffer at the same P-T conditions, the values of the disordering rate constant given by Equation 3 were then corrected in the program CRATE at each step by a factor of $(10^{-24}/10^{-32})^{1/6}$. The obtained cooling time constant was η = 0.0566 × 10^{-3} $K^{-1}year^{-1}$ and the resulting cooling rate r = η × $(T_c)^2$ at the closure temperature T_c = 529 °C was ~0.1 °C/day. Error on the cooling rate was evaluated by calculating the minimum and maximum values of r on the basis of one standard deviation (1σ) of the site occupancy data. These values were ~0.04 and ~0.23 °C/day, respectively. In order to also estimate the possible error on the cooling rate associated with the change in oxygen fugacity, a calculation of η was performed by imposing n = 5.5 and n = 6.5 for the exponent of (fO_2). This caused a variation of cooling rate r from ~0.13 °C/day to ~0.08 °C/day, widely within the uncertainty due to error on the site occupancy data.

To place our result in a wider context, we report the cooling rate of orthopyroxene samples from well-characterized geological contexts obtained by applying the procedure described above to data from literature:

- A cooling rate of 1.4 °C/day at T_c 619 °C was calculated on orthopyroxene N. 1 from Old Homestead 001 howardite (Domeneghetti et al. 2000). The high T_c value measured on this sample had been interpreted by these authors as indicative of high T quenching due to "either impact excavation of material from still hot plutonic rocks or heating of the cumulate material due to impact events."
- A cooling rate of ~65 °C/day at the T_c of 750 °C was calculated on orthopyroxene V6 from the upper part of quenched volcanic lava (Bertolo and Nimis 1993).
- A cooling rate in the order of ~1 °C/Myr at a T_c of 340 °C was measured by Stimpfl et al. (2005) on orthopyroxene from the British Columbia Central Gneissic Complex and reflects low-temperature cooling in a metamorphic environment.

Given the complex geological history recorded by this sample (Harvey and McSween 1996; Treiman 1998, 2003; Koziol 2004), interpretation of cooling rate results for

Table 4. Atomic positions ($\times 10^4$) and atomic displacement parameters (Å$^2 \times 10^3$) of sample ALH 84001 N.1.

	x	y	z	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
SiA	2713(1)	3409(1)	502(2)	19(1)	22(1)	19(1)	17(1)	0(1)	1(1)	−1(1)
SiB	4743(1)	3371(1)	7965(2)	20(1)	22(1)	19(1)	18(1)	0(1)	0(1)	0(1)
O1A	1835(1)	3387(3)	410(5)	21(1)	24(1)	20(1)	19(1)	−1(1)	1(1)	0(1)
O1B	5626(1)	3378(3)	7985(5)	21(1)	23(1)	22(1)	18(1)	1(1)	0(1)	−1(1)
O2A	3110(1)	5008(3)	505(5)	23(1)	28(1)	20(1)	21(1)	1(1)	0(1)	−3(1)
O2B	4340(2)	4854(3)	6949(5)	24(1)	28(1)	22(1)	21(1)	3(1)	1(1)	2(1)
O3A	3024(1)	2299(3)	−1767(5)	24(1)	26(1)	27(1)	19(1)	−5(1)	0(1)	−1(1)
O3B	4474(1)	2011(3)	5944(5)	23(1)	25(1)	24(1)	20(1)	−2(1)	1(1)	−1(1)
M1	3755(1)	6545(1)	8720(2)	21(1)	25(1)	20(1)	18(1)	1(1)	−1(1)	0(1)
M2	3780(1)	4828(1)	3661(2)	23(1)	27(1)	24(1)	19(1)	−1(1)	−2(1)	−2(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U^{11}+...2hka^*b^*U^{12})$.

orthopyroxenite ALH 84001 is not straightforward. In a detailed and careful revision, Treiman (1998) identified and characterized at least four distinct impact events (I1 to I4–I5). After the thermal metamorphism (Cγ) that annealed the granular bands developed during the I1 event, ALH 84001 underwent two (I2 and I3) shock heating events (Treiman 1998) in the temperature range in which the orthopyroxene geospeedometer is sensitive. Subsequent (I4 and I5) impact events produced faulting at temperatures too low (Treiman 1998) to affect the orthopyroxene Fe^{2+}-Mg ordering state.

It is important to remember that the Fe^{2+}-Mg exchange in orthopyroxene is a reversible reaction. Even a highly ordered orthopyroxene, resulting from very slow cooling of the host rock during geological times, can be rapidly disordered if its T_c is exceeded. Once disordered, orthopyroxene loses its memory of its previous ordering state and the final degree of order that it records depends only on the cooling history that follows the disordering event. Compressional shock heating associated with I2 converted some of ALH 84001 feldspar to glass, while heating associated with I3 produced melting and vesiculation of feldspathic glass and films of pyroxene-composition glasses (Treiman 2003). These data indicate that during I3, the rock was heated to temperatures hotter than during I2. It follows that the measured Fe^{2+}-Mg intracrystalline ordering state measured in ALH 84001 orthopyroxene can be ascribed to I3 and provides constraints on this thermal stage. Impact products associated to I3 imply temperatures as high as 800–900 °C (Bischoff and Stöffler 1992). We have calculated that at temperatures of 900, 800, and 600 °C, the time required to disorder to equilibrium a very highly ordered orthopyroxene (e.g., an orthopyroxene slowly cooled in a plutonic environment) is on the order of 3 min, 36 min, and 52 days, respectively. This calculation was carried out for an orthopyroxene with ALH 84001 composition, at the QFM buffer condition, on the basis of Mueller's (1967, 1969) model using the above-quoted Equations 2 and 3. Our calculation indicates two things. First, at high enough temperatures, Fe^{2+}-Mg ordering in orthopyroxene can indeed be reset in geologically negligible times, consistent with an instantaneous shock-heating event. Second, even a heating event at lower temperatures (i.e., ~600 °C) would have started the orthopyroxene geospeedometer. The cooling time constant $\eta = 0.0566 \times 10^{-3}$ K^{-1}year^{-1} retrieved for ALH 84001 orthopyroxene provides a cooling rate value of ~0.12°C/day at 600 °C. It follows that the time required by the sample to cool by even only 10 °C is about 80 days, a time sufficient at this T to reset any previous Fe^{2+}-Mg order degree.

On the basis of petrographic relationships, Treiman (1998) observed that I3 postdated the formation of carbonate globules and suggested that iron-rich carbonates were decomposed to submicron magnetite during heating associated with this shock event. Treiman (2003) hypothesized that heating was not much higher than 430 °C and lasted a relatively short time geologically to allow preservation in carbonate globules of the chemical zoning, which predates I3. Treiman (2003) also suggested that indicators of higher temperatures such as feldspathic and pyroxene-composition melts could represent local effects of stress concentration. As the T_c recorded by orthopyroxene represents a temperature certainly reached (and very likely exceeded) during the shock heating event, our data indicate that shock temperature associated to I3 was not lower, and was likely higher, than 529 °C. Our data can only provide the minimum value for the shock temperature; they do not constrain the maximum post-shock heating of the sample. For this reason the orthopyroxene T_c ~529 °C is not in contrast with the possibility that during I3 the rock experienced temperatures as high as 800–900 °C, as suggested by the formation of feldspathic melts (Bischoff and Stöffler 1992). Assuming that ALH 84001 was indeed heated at ~800 °C, we can use the cooling time constant $\eta = 0.0566 \times 10^{-3}$ K^{-1}year^{-1} retrieved by the Fe^{2+}-Mg ordering state of the orthopyroxene to calculate the time required to cool the sample from 800 to 600 °C. The result of this calculation is about 4 years. Such prolonged annealing at high temperature is clearly incompatible with preservation of compositional zoning in carbonates (Kent et al. 2001), and possibly with the preservation of carbonates themselves. It is logical to infer that during I3 either the whole rock never reached such high temperatures or, if it did, the heating and cooling rate had to be fast enough to leave carbonates undisturbed. Our data cannot discriminate between these alternatives. However, if heating at high T is indeed required to account for melting, mobilization, and vesiculation of felspathic glass (Treiman 1998), we must suppose that after this event the sample was first rapidly quenched to $T < 600$ °C and then cooled at the rate recorded by the orthopyroxene. Kent et al. (2001) argued that up to temperatures as high as 600 °C, cooling rates of the order of 10^7 °C/Myr are sufficiently rapid to preserve carbonate compositional heterogeneity at the length scale of variations found in ALH 84001. The cooling rate of ~3.5×10^7 °C/Myr and the T_c of 529 °C we retrieved from the measured orthopyroxene Fe^{2+}-Mg ordering state do match the physical conditions required by experimental constraints for survival of the observed chemical zoning of ALH 84001 carbonates.

The thermal history deduced from ALH 84001 orthopyroxene Fe^{2+}-Mg ordering state does not conflict with Golden et al.'s (2004) experiments on thermal decomposition of Fe-rich carbonates. These authors showed that the whisker-shaped magnetite crystals produced by thermal decomposition of Fe-rich carbonates heated for about 1 hr at 550 °C and then quenched are similar to those formed in ALH 84001 during shock and show "all the defining characteristics of biogenic MV-1 magnetite, except the crystal shape" (Golden et al. 2004). The final Fe^{2+}-Mg ordering state of the orthopyroxene indicates that temperatures (≥529 °C) and fast cooling rate (~3.5×10^7 °C/Myr) conditions similar to those required for the formation of whisker-shaped magnetite (Golden et al. 2004) occurred on Mars. No experimental runs at temperatures higher than 550 °C are reported in Golden et al. (2004), so we cannot evaluate the effects of higher temperatures in this experimental context. Dissociation of ferrous carbonates and formation of fine-grained magnetite at high temperature (~1100 °C) are described in Zolotov and Shock (2000), suggesting that high-temperature (800–900 °C) shock heating hypothesized for I3 cannot be excluded and might actually have triggered the decomposition of carbonates.

Cooling rate alone cannot be used to calculate the precise depth at which the sample was cooling at around 530 °C because this calculation depends heavily on the choice of boundary conditions (Sears et al. 1997; Warren et al. 1991; Vorsteen and Schellschmidt 2003), which are fairly unconstrained in the present case. However the fast cooling recorded by ALH 84001 orthopyroxene indicates a location very close to the surface of the cooling body (on the order of a few meters). Assuming 600 °C as the initial temperature of the fallout-ejecta blanket, 0 °C as the temperature for near-surface rock on Mars (Treiman 2003) and the thermal diffusivity of 2.32 m^2/yr suggested by Warren et al. (1991) for lunar megaregolith, we calculated that the cooling rate of ~0.1 °C/day at the T_c of ~530 °C would correspond to a burial depth of about 6 m. Under these conditions, the rock would have taken about 200 yr to cool down to ~10 °C. We want to stress that the thermal diffusivity chosen for this calculation is highly arbitrary, because no such data exist on Martian regolith. These results do not contrast with the hypothesis that, after I3, the rock was at pressure greater than atmospheric and that cooling lasted a few centuries (Treiman 2003). It is also consistent with the observation that, after I3, the rock never experienced temperatures above 350–500 °C (Weiss et al. 2002; Fritz et al. 2005) for even very short times.

A plausible scenario is that after carbonate formation on the Martian surface, the ALH 84001 rock was shock-heated and quenched when launched into the atmosphere, and then once it fell back to the surface, was covered by, or formed part of, a fallout-ejecta blanket.

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