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Temperatures on Mars from $^{40}Ar/^{39}Ar$ thermochronology of ALH84001

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Abstract

The thermal history of Martian meteorite ALH84001 has critical implications for its petrological and deformational history, the age of its trapped atmospheric gases, the timing of the Martian dynamo, and possibly the evolution of Martian surface temperatures during the last 4 billion years (Gyr). Feldspathic glass in ALH84001 has been dated using $^{40}K/^{40}Ar$ and $^{40}Ar/^{39}Ar$ chronometry by several laboratories. There is general agreement that these chronometers were last reset sometime between 3.9 and 4.3 billion years ago (Ga). Using the $^{40}Ar/^{39}Ar$ data from Bogard and Garrison [Meteorit. Planet. Sci. 34 (1999) 451–473] to model several limiting thermal histories of the meteorite, here we show that most of ALH84001 feldspathic glass has probably not been heated to more than $\sim$350–500°C and shocked to peak pressures $\sim>1$ GPa since the glass was last melted. This indicates that most of ALH84001 has been well below these temperatures since 3.9–4.3 Ga. Since these temperatures are below the Curie point of magnetite, much of the magnetization recently identified in ALH84001 carbonate [Weiss et al., Earth Planet. Sci. Lett. this issue] must have been acquired by $\sim$4 Ga. This also provides an explanation for why ALH84001 contains a sample of an apparently ancient Martian atmosphere that is less evolved relative to that on present-day Mars. Our calculations also suggest that for the last 4 Gyr, average surface temperatures on Mars may not have been much higher than the present cold conditions.

Keywords: Mars; ALH84001; Martian meteorites; argon; thermochronology; temperature; paleomagnetism; climate change

1. Introduction

The meteorite ALH84001 is an orthopyroxene cumulate from Mars with a Sm/Nd age of 4.50 Ga [3,4]. This extreme age – the oldest known for any planetary rock – is reflected by the multiple episodes of intense deformation recorded by the meteorite's petrofabric [5]. During the first few hundred million years of its history, ALH84001 was partially melted and fractured by several shock events. In some of these fractures formed zoned carbonate blebs with Rb/Sr and Pb/Pb ages of 3.90 ± 0.04 Ga and 4.04 ± 0.1 Ga, respectively [6] (although the Rb/Sr dates are controversial [7]). Feldspathic glass, which makes up $\sim$1 wt% of the meteorite, is ubiquitously distributed throughout the rock and very commonly sur-

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rounds carbonates [5]. The texture, shape, and structure of this glass indicate that it was shocked and mobilized (and probably melted) at least once after the carbonate formed [2,5,8–10]. The last such event was labeled 'D3' by Treiman [5], during which ALH84001 apparently experienced peak pressures of 40–60 GPa [5,11] and post-shock temperatures of 400–1000°C [10–12].

Several laboratories have conducted $^{40}K/^{40}Ar$ and $^{40}Ar/^{39}Ar$ dating of ALH84001 using stepped heating of bulk grains [1,13–17] and by laser probe [17]. Essentially all experimenters agree that the dominant carrier of K and radiogenic ^{40}Ar in ALH84001 is feldspathic glass. There is also near universal agreement that the meteorite last completely degassed ^{40}Ar sometime between 3.9 and 4.3 Ga (depending on the composition assumed for trapped Ar). On the other hand, laser probe dating [17] has identified a few locations in the meteorite having $^{40}Ar/^{39}Ar$ ages of 4.4 Ga. This suggests that while much of the meteorite was strongly heated sometime during 3.9–4.3 Ga, isolated locations may have escaped heating since 4.4 Ga, possibly due to the spatially heterogeneous nature of shock heating [18]. The coincidence of the main ~4 Ga population of $^{40}Ar/^{39}Ar$ ages with those of impact glasses from the lunar highlands provides the first direct evidence that Mars may have experienced a heavy bombardment of impactors contemporaneous with the lunar cataclysm [19].

Here we demonstrate that the $^{40}Ar/^{39}Ar$ chronometer of ALH84001 was probably last reset by the D3 shock event that mobilized its feldspathic glass. This was presumably the result of an impact on the Martian surface. We show that ever since this time, the meteorite has experienced very mild temperatures and shock pressures.

2. Thermochronology

Using the ^{39}Ar release data of Bogard and Garrison [1], we modeled (following the methods of [20]) the temperature dependence of the diffusion coefficient of Ar through ALH84001 feldspathic glass using an Arrhenius relationship, $D(T) = D_0/a^2 \exp(-E_a/RT)$, for characteristic constants D_0/a^2, E_a, and the gas constant R (Fig. 1). From this we derive best-fit values of $\ln(D_0/a^2) = -1.9 \pm 0.2$ $\ln(s^{-1})$ and $E_a = 76.8 \pm 1.3$ kJ mol^{-1} (these uncertainties are formal errors from the regression analysis only), with a linear correlation coefficient $r^2 = 0.998$ (number of heating steps $n = 12$). In the calculations presented below, we assume that this Arrhenius relationship has held for ALH84001 glass since it was last mobilized during the D3 deformational event and that the diffusion domain size a is constant for all time in our calculations.

Because ^{39}Ar resides in several distinct phases [1], we used ^{39}Ar released only from the high K/Ca phases (i.e., the 200–850°C steps) in our calculation of $\ln(D/a^2)_i$ for each step i (Fig. 1). Following the conclusions of Bogard and Garrison [1] and Turner et al. [17], we assume that ^{39}Ar released during steps > 850°C (which presents as anomalously low ages in the age spectrum between 80 and 92% cumulative gas release; see Fig. 2) is the product of recoil, and so we excluded these from the regression (Fig. 1) We also excluded the three steps < 450°C from the regression (Fig. 1) because some of that gas was possibly derived from a recently precipitated weathering product [1]. Inclusion of the latter values in the regression would have a negligible effect upon our conclusions.

The Arrhenius relationship is more sensitive to which steps we include in our calculation of $\ln(D/a^2)$ [20]. For instance, if we exclude the steps < 450°C from the calculation, our best-fit values become $\ln(D_0/a^2) = 1.3 \pm 0.4$ $\ln(s^{-1})$ and $E_a = 103 \pm 2.6$ kJ mol^{-1}. In their $^{40}Ar/^{39}Ar$ experiments on ALH84001, Turner et al. [17] obtained a similar value for E_a and also noted its dependence on the low temperature release. We do not favor the latter values since they rely on less of the measured data: the latter calculation entirely ignores the first three release steps, requires excluding three high temperature steps from the regression to maintain reasonable linearity, and provides a poorer fit to the resulting regression ($r^2 = 0.995$; $n = 9$).

Our goal is to determine the maximum temperature the meteorite experienced during the last 4 billion years (Gyr). The primary observational

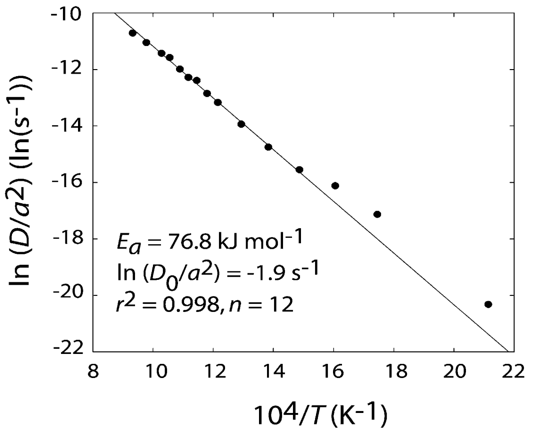

Fig. 1. Arrhenius plot showing the calculated temperature dependence of the diffusion coefficient of ^{39}Ar through ALH84001 feldspathic glass, $D(T)$. Spherical diffusion domain geometry. Plotted is the natural logarithm of the ratio of D to the squared diffusion domain radius, a^2, as a function of inverse temperature. Data were taken from the stepwise heating experiments on ALH84001,113 by Bogard and Garrison [1] up to the 850°C step. The solid line is our best-fit Arrhenius relationship excluding the three low temperature points (see text for discussion), which has an ordinate-intercept of $\ln(D_0/a^2) = -1.9 \pm 0.2$ ln(s^{-1}), a slope of $E_a = 76.8 \pm 1.3$ kJ mol^{-1}, and a linear correlation coefficient $r^2 = 0.998$.

limit is the fraction of 'missing' radiogenic ^{40}Ar that has been diffusively lost from the feldspathic diffusion domain(s). To quantify this fraction, we forward modeled the distribution of Ar in the glass using the previously derived Arrhenius relationship (Fig. 1). We assumed the idealized case of a uniform size distribution of spherical diffusion domains containing a uniform distribution of ^{39}Ar (produced from experimental irradiation of K) but which had recently (within the last few million years) diffusively lost some fraction (1%, 5%, or 10%) of the total ingrown ^{40}Ar. We then put these grains through a simulated stepwise heating schedule. Based on the diffusion parameters determined from Bogard and Garrison's [1] data (discussed above) and the same heating schedule of their experiment, we calculated the expected ^{40}Ar/^{39}Ar ratio as a function of cumulative ^{39}Ar release fraction. A comparison of the model results with the measured ratios (Fig. 2) demonstrates that curves corresponding to $\geq 5\%$ gas loss (solid blue and red curves) reach a plateau at significantly higher cumulative release fractions than do the data (black diamonds). This conclusion is insensitive to the choice of age to which the data are normalized. We conclude that $< 5\%$ missing ^{40}Ar fraction most closely matches the observations. A similar result is obtained if diffusive loss of ^{40}Ar had instead been assumed to occur 3.5 Ga and had been followed by 3.5 Gyr of radiogenic ingrowth (Fig. 2, dashed blue curve).

Before continuing, we discuss the sensitivity of this conclusion to the imperfections in the age spectrum. Firstly, the three points with cumulative ^{39}Ar release between 80 and 92% (age ~3.5 Ga) in Fig. 2 are thought to reflect a recoil effect due to the juxtaposition of a K-rich and K-poor phase [1]. The above conclusions drawn from Fig. 2 are therefore based on the comparison between

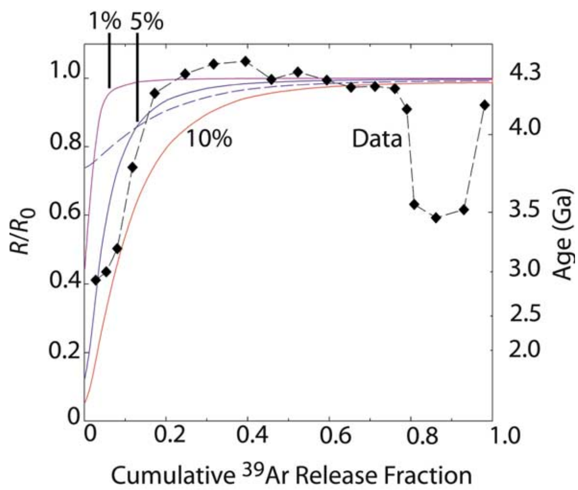

Fig. 2. Model age spectra for various degrees of diffusive ^{40}Ar loss and a uniform distribution of ^{39}Ar. Shown is the ^{40}Ar/^{39}Ar ratio, R (normalized to the ratio at the center of the diffusion domain, R_0), plotted as a function of cumulative ^{39}Ar release fraction. Also plotted is the ^{40}Ar/^{39}Ar spectrum for ALH84001,113 measured by Bogard and Garrison [1], normalized to the ^{40}Ar/^{39}Ar ratio of the mean plateau age of 4.3 Ga. Included are the ^{40}Ar/^{39}Ar ages reported in [1] for reference. The color of each solid curve corresponds to a different amount of radiogenic ^{40}Ar lost at 15 Ma (expressed as a fraction of the total amount of initial radiogenic ^{40}Ar): purple = 1% lost, blue = 5% lost, red = 10% lost. For comparison, we include the expected release pattern for 5% lost ^{40}Ar, assuming instead that the loss event occurred at 3.5 Ga ago and was followed by 3.5 Gyr of quantitatively retained radiogenic ingrowth (dashed blue curve).

our model and the $^{40}Ar/^{39}Ar$ observations for cumulative release fractions less than $\sim$80%. Secondly, although some ^{40}Ar may have been inherited by ALH84001 as a result of weathering in Antarctica, much of the ^{40}Ar from the outer regions of the feldspar diffusion domains was almost certainly lost to surrounding pyroxene during recoil [1]. For this reason, we conservatively estimate that less than 5% of the total ^{40}Ar in the meteorite has been lost since the $^{40}Ar/^{39}Ar$ chronometer was reset. This places stringent limits on the amount of heating that ALH84001 can have experienced since 4 Ga.

We used the Ar release data of Bogard and Garrison [1] to estimate the amount of gas that would be lost during several hypothetical thermal histories. Given the lack of geologic and historical context for the meteorite, we first examined the most stringent scenario, in which the meteorite (approximated as a sphere with a preatmospheric radius of $\sim$0.2 m [15,21]) was exposed to an elevated temperature T_0 near the time of its ejection from Mars 15 million years ago (Ma). We assumed that only the meteorite's volume was instantly heated to T_0 while its surroundings remained initially at ambient Martian surface temperatures ($\sim$210 K). We then calculated the central temperature of the rock as a function of time while it conductively cooled, using one of two different thermal boundary conditions. Firstly, to approximate cooling during shallow ($<$1 km) burial in the regolith, we assumed an infinite surrounding medium of composition similar to the meteorite and initially at 210 K. Secondly, to approximate cooling in space or on the Martian surface, we assumed a Stefan–Boltzmann radiative boundary condition at the meteorite's surface (taking an emissivity of $\sim$0.93 and a solar insolation equilibrium temperature of 210 K), with conductive heat transport in its interior. For these calculations we used a thermal diffusivity of 10^{-6} m^2 s^{-1}, a specific heat of 815 J kg^{-1} K^{-1}, and a density of 3300 kg m^{-3}, typical of $MgSiO_3$. The conduction-only scenario has an analytic solution [22], while the combined conduction–radiation scenario required numerical integration of the diffusion equation. Under both boundary conditions, the meteorite cools at roughly the same rate to near ambient temperatures within a couple of days (Fig. 3).

Such fast cooling prevents calculation of a meaningful closure temperature for Ar diffusion using Dodson's method [23]. As a result, we directly modeled the effects of a thermal pulse on the Ar content of ALH84001. For each of these thermal boundary conditions, the measured ^{40}Ar diffusion parameters, and for several different values of T_0, we calculated the radial distribution of ^{40}Ar remaining after the rock had cooled to ambient Martian surface temperatures. These computations were implemented using a program adapted from a (U–Th)/He thermochronology code developed by Wolf et al. [24]. We assumed a uniform size distribution of spherical feldspathic grains each containing an initially spatially uniform distribution of ^{40}Ar and with the thermal diffusivity as measured (Fig. 1). Compared to a uniform distribution of grain sizes, a lognormal distribution of the same mean and with a variance of 0.4–0.6 (the best-fit size distribution found by Turner et al. [17]) will require slightly less (but nearly identical) time to degas the small amounts ($<$10%) of total ^{40}Ar considered here [25]. Because no more than $\sim$5% of the gas in the mete-

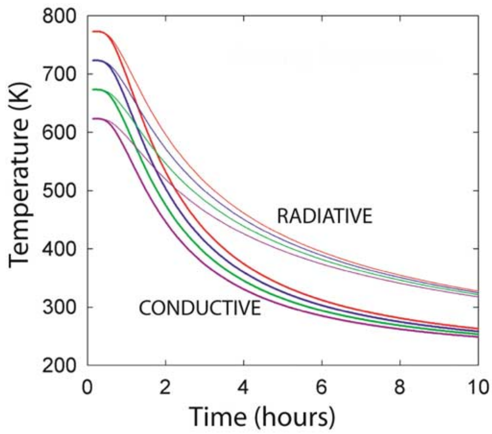

Fig. 3. Thermal diffusion calculations showing the temporal evolution of the central temperature of ALH84001 during cooling from several initial temperatures. The color of each curve corresponds to a specific initial pulse temperature T_0: red = 500°C, blue = 450°C, green = 400°C, and purple = 350°C. The bold and fine curves were calculated assuming a conductive and a radiative boundary condition, respectively (see text).

orite can be lost during the thermal pulse (Fig. 2), these calculations (solid curves in Fig. 4) demonstrate that the maximum temperature of the thermal pulse at 15 Ma is ~350°C. If we move the hypothetical thermal pulse back to an earlier time in the meteorite's history, there will be less ^{40}Ar available to be degassed, and so higher values of T_0 for earlier thermal events are consistent with the 5% loss criterion. In particular, our calculations show that thermal pulses with $T_0 > 400$°C at 2 Ga will also lead to $>5\%$ ^{40}Ar loss, as will pulses with $T_0 > 500$°C at 3.5 Ga (dashed curves in Fig. 4). These results are not sensitive to the method by which we calculated the Arrhenius relationship (e.g., whether or not we included the first three temperature steps in calculating D/a^2).

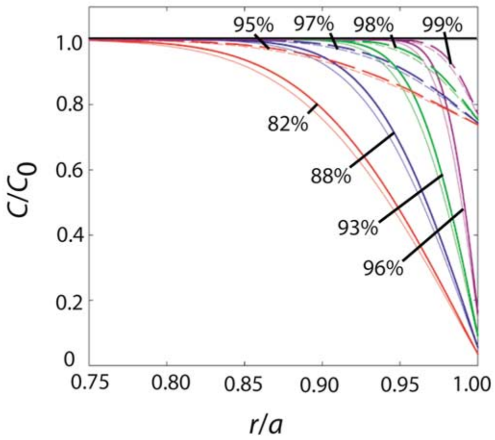

Fig. 4. Thermochronology calculations showing radial distribution of radiogenic ^{40}Ar in spherical ALH84001 feldspar diffusion domains after the meteorite cooled from various starting temperatures (Fig. 3). Shown is the ^{40}Ar concentration, C (normalized to the initial concentration at the center of the diffusion domain, C_0), at various radial distances from the center of the diffusion domain, r (normalized to the diameter of the domain, a). For these calculations we have assumed an initially uniform distribution of ^{40}Ar prior to the thermal pulse. The solid and dashed curves were calculated assuming the thermal pulse occurred at within the last few million years and at 3.5 Ga, respectively. Bold and fine curves were calculated assuming a conductive and a radiative boundary condition, respectively. The color of each curve corresponds to a specific initial pulse temperature T_0: red = 500°C, blue = 450°C, green = 400°C, and purple = 350°C. The initial gas distribution prior to heating is shown by the solid horizontal black line. The colored curves were calculated by inputting the corresponding thermal history (Fig. 3) into an Ar diffusion program (adapted from the (U–Th)/He thermochronology code of Wolf et al. [24]). The number next to each thick line is the total fraction of remaining ^{40}Ar in the grains (i.e., integral of the radial fraction of gas over the entire grain volume) following cooling under the conductive boundary condition.

These are upper limits on the temperatures that ALH84001 has experienced during the last 4 Gyr for several reasons. Firstly, if we had instead assumed that a volume of rock larger than the meteorite was heated to T_0, the cooling time (and therefore ^{40}Ar loss) would be larger (and the maximum temperature lower) than that estimated here. Secondly, we neglected the very significant ^{40}Ar loss that the meteorite experienced while at equilibrium temperatures during its 4 Gyr residence on Mars, 15 million years (Myr) in space, and 11000 years on Earth. It is difficult to estimate precisely how much additional gas was lost during these periods, during which the meteorite's temperature history is not precisely known. A second difficulty comes from the likelihood that the temperatures experienced during much of these periods were several hundred °C below those for which the Arrhenius coefficients were measured [1,17]. Nevertheless, using a linear extrapolation of the derived Arrhenius relationship (Fig. 1), we estimated the amount of ^{40}Ar that should have been degassed from the meteorite during the last 15 Myr in space and on Earth. We found that, depending on the orbital path taken by the meteorite from Mars to Earth, the Ar loss could have been anywhere from ~4% (in the limiting scenario in which the meteorite spent nearly all of the last 15 Myr at or beyond Mars' orbit) to several tens of percent or more (if it spent more of this period at smaller semimajor axes). Because the meteorite has lost less than 5% of its ^{40}Ar (Fig. 2), this strongly suggests that the actual maximum temperature experienced by the meteorite during any conductively cooling thermal pulse in the last 4 Gyr is well below (conceivably several hundred °C below) our nominal 350–500°C limit.

We now consider the possibility that ALH-84001 was heated sometime in the last ~4 Gyr by a high temperature shock event. Much (but usually not all) of the temperature rise that occurs during a shock can cool adiabatically much faster than a conductively cooling thermal pulse to the same peak temperature [26]. In any case, ALH84001 probably has not been significantly shock-heated because the feldspathic glass in the meteorite is very rarely fractured. The lack of fractures requires that since it was last melted, the glass could not have been differentially stressed at pressures exceeding its tensile strength ($\sim$1 GPa) [27,28] unless it reached pressures sufficient for the production of diaplectic glass ($\sim$30–35 GPa) [11]. However, such pressures would be associated with post-shock temperatures exceeding $\sim$250°C [11]. Since the meteorite would then have to conductively cool from these post-shock temperatures, our previous conductive calculations render them (and the shocks that produce them) unlikely. There is also no other textural or petrological evidence in the meteorite for any shock events younger than the last glass flow event [5]. This means that most of ALH-84001 probably has experienced negligible shock-heating since this event.

3. Implications

The glass and any nearby carbonates probably have not experienced peak shock pressures above $\sim$1 GPa and temperatures above $\sim$350–500°C for even very short time periods during the last 4 Gyr. Since these temperatures are below the Curie point of magnetite, much of the magnetization measured in ALH84001 carbonates intimately associated with the glass [2] must have been acquired by $\sim$4 Ga. This is consistent with the conclusion of Weiss et al. [29] (and the breccia test by Kirschvink et al. [30]) that ALH84001 was not heated above $\sim$40°C during the last 15 Ma. This also provides an explanation for why the isotopic composition of Martian atmospheric Xe, N, H, and Ar trapped in ALH84001 resembles that expected for an atmosphere less evolved than that presently on Mars [31–38]. Given that a shock of at least several tens of GPa is probably necessary for shock-implantation of the large amount of atmospheric gases in ALH84001 [39,40], our results strongly support suggestions [31–38] that the meteorite contains a sample of 4-Gyr-old Martian atmosphere. That these gases are enriched in light isotopes of H and N relative to present-day values supports the hypothesis that significant atmospheric loss has occurred on Mars since 4 Ga.

Given the very high and probably long-lived post-shock temperatures that followed the glass-mobilization D3 event, our diffusion calculations suggest that it was responsible for resetting the $^{40}Ar/^{39}Ar$ chronometer throughout most of the meteorite at $\sim$4 Ga. That the D3 event (and not an earlier deformational event) was capable of resetting the chronometer is also supported by the lack of a second high temperature plateau of different age in the many different age spectra that have been measured [1,16,17]. However, note that if the subpopulation of 4.4 Ga laser probe dates is not an artifact but instead is reflective of isolated locations in ALH84001 that escaped late heating [17], the D3 event may not have completely reset the $^{40}Ar/^{39}Ar$ chronometer everywhere in the meteorite.

That even one of the two dozen known Martian meteorites has been this cool for so long gives evidence of great differences in the extent and duration of igneous and tectonic processes on Earth and Mars. Perhaps even more remarkably, using a linear extrapolation of the Arrhenius relationship down to low temperatures, we find that ALH84001 could not have been held at a constant temperature exceeding -70 ± 4°C during the last 4 Gyr prior to its ejection from Mars (otherwise, it would have lost more than 5% of its ^{40}Ar). Any temperature excursions during the last 4 Gyr to 0°C as short-lived as $\sim 10^4$-10^5 yr are also contradicted. It is important to note that the quoted uncertainty 4°C is estimated from the formal errors in the Arrhenius relationship yielded by the regression analysis, and does not include the very large uncertainty resulting from the possibility that our bold extrapolation of D (through six orders of magnitude) is inappropriate. In particular, had we used our alternate (but less favored) Arrhenius relationship derived from the low temperature release data (see Section 2), the limiting temperature becomes -25°C.

Interestingly, this limiting -70°C temperature is near the center of the present-day range of average surface temperatures ($\sim$ -90 to -40°C) in

Martian mid to high latitudes. The likelihood that Mars' obliquity (and surface temperatures) have periodically reached high values [41] can be reconciled with these constraints if during the last 4 Ga, ALH84001 was buried at depths $> \sim 0.1$–1 km (depending on its latitude and the frequency of the obliquity oscillations), where it would be shielded from the obliquity-induced, seasonal, and diurnal thermal waves. In summary, if our extrapolation of the diffusion coefficient is not grossly inaccurate, this suggests that for most of the last 4 Gyr, average temperatures near the Martian surface may not have been significantly warmer than those today. Future studies of ALH84001 using thermochronometers with closure temperatures lower than that of $^{40}Ar/^{39}Ar$ (e.g., (U–Th)/He) could rigorously test this possibility.

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