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Note

Trapped Ar isotopes in meteorite ALH 84001 indicate Mars did not have a thick ancient atmosphere

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ABSTRACT

Water is not currently stable in liquid form on the martian surface due to the present mean atmospheric pressure of ~7 mbar and mean global temperature of ~220 K. However, geomorphic features and hydrated mineral assemblages suggest that Mars' climate was once warmer and liquid water flowed on the surface. These observations may indicate a substantially more massive atmosphere in the past, but there have been few observational constraints on paleoatmospheric pressures. Here we show how the $^{40}Ar/^{36}Ar$ ratios of trapped gases within martian meteorite ALH 84001 constrain paleoatmospheric pressure on Mars during the Noachian era [~4.56–3.8 billion years (Ga)]. Our model indicates that atmospheric pressures did not exceed ~1.5 bar during the first 400 million years (Ma) of the Noachian era, and were <400 mbar by 4.16 Ga. Such pressures of CO_2 are only sufficient to stabilize liquid water on Mars' surface at low latitudes during seasonally warm periods. Other greenhouse gases like SO_2 and water vapor may have played an important role in intermittently stabilizing liquid water at higher latitudes following major volcanic eruptions or impact events.

1. Introduction

The composition and mass of the ancient martian atmosphere are key parameters of planetary evolution that remain poorly understood. Radiative transfer models suggest that a greater pressures of greenhouse gases in the past (e.g., >5 bars of CO_2) were necessary to sustain surface temperatures above freezing for prolonged durations (Jakosky and Phillips, 2001; Pepin, 1994; Colaprete and Toon, 2003; Pollack et al., 1987; Yung et al., 1997). Alternatively, large impacts may have vaporized subsurface volatiles and generated relatively brief periods of warm and wet conditions (e.g., 10^2–10^3 years; Segura et al., 2002), which may explain why a decrease in fluvial erosion appears to coincide with the end of the heavy impact bombardment (Catling and Leovy, 2007). Both explanations imply climate conditions during the Noachian era that were significantly different from the present. However, whereas prolonged periods of high concentrations of greenhouse gases implicate warm and wet surface environments conducive to life, intermittent impact-driven greenhouse events do not.

Observational constraints on past climate conditions on Mars are limited. The scarcity of carbonate minerals (Bandfield, 2002; Bibring et al., 2006; Murchie et al., 2009) (expected to form in low-SO_2 aqueous environments) and the apparently low partial pressures of CO_2 required to explain the alteration of Noachian surface rocks to clay minerals (0.001–0.01 bar; Chevrier et al., 2007) suggest that a dense CO_2-rich atmosphere did not persist throughout the Noachian. The identification of sulfate deposits in the martian regolith (Arvidson et al., 2005; Gendrin et al., 2005; Squyres et al., 2004) indicates that atmospheric SO_2 and H_2S may have contributed to greenhouse warming. Modest influxes of SO_2 and H_2S (e.g., $\sim 2 \times 10^{-6}$ bar) in the presence of only 50 mbar CO_2 can promote transient periods of warm, wet conditions (Halevy et al., 2007; Johnson et al., 2008). Despite these observations, whether a dense, CO_2-rich atmosphere ever existed and the extent to which other greenhouse gases contributed to warming remain poorly understood.

Martian meteorites contain trapped atmospheric gases (Bogard et al., 2001) that provide chemical constraints on past atmospheric conditions. Cassata et al. (2010) identified a trapped argon (Ar) component within maskelynite in the 4.16 ± 0.04 Ga old martian meteorite ALH 84001 with an $^{40}Ar/^{36}Ar$ ratio of 626 ± 100 (Fig. 1). Here we present the first attempt to use this isotopic composition to constrain atmospheric pressure on Mars between the time of planetary formation and the 4.16 Ga age of the maskelynite. We discuss the implications of these pressure limits for greenhouse warming, atmospheric evolution, and climate on Mars during the Noachian era. Critical to our arguments is the assumption that the trapped argon component identified within maskelynite is atmospheric in origin and was emplaced in the meteorite at 4.16 Ga. The concordance of the maskelynite $^{40}Ar/^{36}Ar$ vs. $^{39}Ar/^{36}Ar$ isochron diagram (Fig. 1) provides strong support for such an interpretation; terrestrial feldspars and glasses with appreciably non-atmospheric trapped components generally fail to produce linear isochron diagrams (discussed in detail in the Supplementary Files).

2. An atmospheric ^{40}Ar evolution model

A comparison of the atmospheric $^{40}Ar/^{36}Ar$ ratios of Earth and Mars reveals significant differences in the evolution of the two atmospheres (Fig. 1). On Earth, the net transport of volatiles from the asthenosphere and lithosphere to the atmosphere has elevated the atmospheric $^{40}Ar/^{36}Ar$ ratio from its primordial ratio of $\sim 10^{-3}$ at 4.56 Ga (Begemann et al., 1976) to the present value of >298 (Lee et al., 2006). Meteorite measurements indicate that on Mars, the atmospheric $^{40}Ar/^{36}Ar$ ratio increased from $\sim 10^{-3}$ at 4.56 Ga, to 626 ± 100 at 4.16 Ga, to the present value of ~1800 (Bogard et al., 2001). Thus, the net effects of martian planetary degassing and late stage planetary accretion increased the martian atmospheric $^{40}Ar/^{36}Ar$ ratio to more than twice the modern ratio on Earth, but over only ~1/10 the duration (~400 Ma). The relatively rapid evolution in the martian atmospheric $^{40}Ar/^{36}Ar$ ratio suggests that one or more of the following is true:

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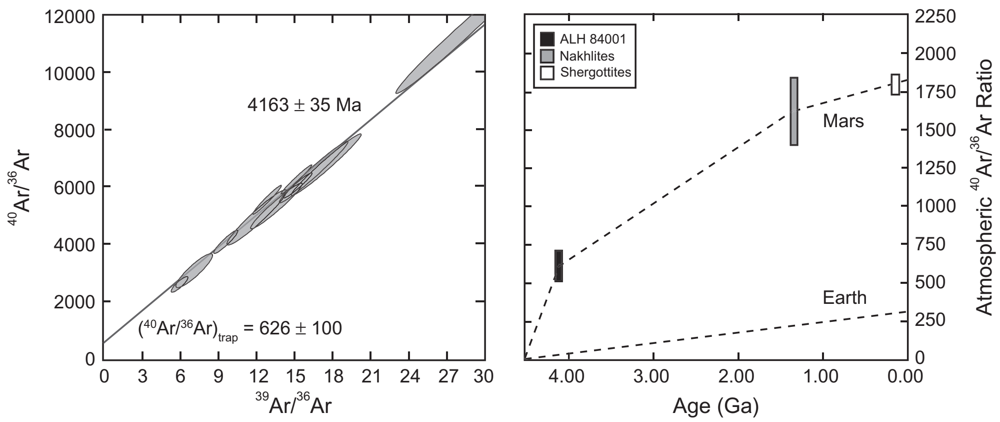

Fig. 1. Left: $^{40}Ar/^{39}Ar$ isochron diagram for maskelynite in ALH 84001-1 [redrafted from Cassata et al. (2010)]. Correlation between the isotope ratios $^{39}Ar/^{36}Ar$ and $^{40}Ar/^{36}Ar$ measured during stepwise degassing of ALH 84001 constrains the non-radiogenic argon component "trapped" in the glass from the *y*-intercept and the age from the slope. The isochron age (4.165 ± 0.035 Ga) is indistinguishable at 2 σ from recently reported Lu–Hf (4.09 ± 0.03 Ga; Lapen et al., 2010) and Pb–Pb (4.074 ± 0.099 Ga; Bouvier et al., 2009) ages. The $^{40}Ar/^{36}Ar$ ratio of the trapped component in ALH 84001 maskelynite is 626 ± 100. Right: Plot of the $^{40}Ar/^{36}Ar$ ratios of trapped Ar components identified in martian meteorites. ALH 84001 and Nakhlite data are from Cassata et al. (2010). Shergottite data are from Bogard et al. (2001). The Nakhlite $^{40}Ar/^{36}Ar$ ratio represents the weighted average of MIL 03346 and Nakhla meteorites (see Supplementary Files). Earth's atmospheric $^{40}Ar/^{36}Ar$ ratio is shown for comparison. Dashed lines linearly connect data points and do not represent the evolution of the atmospheric $^{40}Ar/^{36}Ar$ ratio on Earth or Mars. We have used a young age for Shergottites. However, if the melt veins containing trapped atmospheric gases in EETA 79001 are older (e.g., >4 Ga), as suggested for the age of Shergottites by Bouvier et al. (2009), then the martian atmospheric $^{40}Ar/^{36}Ar$ ratio must have increased even faster than shown in this figure.

(1) the potassium (K) concentration of Mars is greater than Earth, such that significantly more radiogenic ^{40}Ar was generated early on Mars,
(2) the ^{36}Ar concentration of Mars' interior is lower than Earth's, such that extracted magmas had elevated $^{40}Ar/^{36}Ar$ ratios relative to terrestrial magmas of equivalent age and K concentration,
(3) planetary degassing was more efficient on early Mars than Earth, such that a greater proportion of radiogenic ^{40}Ar was delivered from the astheno-lithosphere to the atmosphere, and/or
(4) Mars had a thinner atmosphere than Earth (i.e., less atmospheric ^{36}Ar), such that a given quantity of degassed ^{40}Ar more efficiently elevated the atmospheric $^{40}Ar/^{36}Ar$ ratio.

In this paper, we use published constraints on (1)–(3) to assess whether or not (4) is a viable explanation for Mars' elevated $^{40}Ar/^{36}Ar$ ratio at 4.16 Ga. We simulate planetary degassing under a broad range of atmospheric pressure conditions and explore the resulting evolution in the martian atmospheric $^{40}Ar/^{36}Ar$ ratio during the Noachian. Our objective is to place bounds on atmospheric pressures during the first ~400 Ma of martian history that are consistent with an $^{40}Ar/^{36}Ar$ ratio of 626 ± 100 at 4.16 Ga. We begin with the following postulates:

(1) Mars was assembled from bodies that had an initial inventory of volatiles with $^{40}Ar/^{36}Ar < 10^{-3}$ (Begemann et al., 1976).
(2) Planetary degassing and meteorite accretion added both radiogenic volatiles (^{40}Ar) and non-radiogenic volatiles (^{36}Ar, N_2, and CO_2) to the atmosphere.
(3) Atmospheric loss due to impact erosion removed volatiles, but did not fractionate ^{36}Ar and ^{40}Ar (Brain and Jakosky, 1998; Melosh and Vickery, 1989).
(4) At 4.16 ± 0.04 Ga the atmospheric $^{40}Ar/^{36}Ar$ ratio was 626 ± 100, as indicated by the trapped component in ALH 84001 maskelynite (Cassata et al., 2010).

Under these conditions, the atmospheric molar abundance of Ar isotope X varies through time according to the following equation:

$$\frac{d^{X}Ar}{dt} = N_X(t) - \left({}^{X}Ar\frac{L(t)}{P(t)}\right), \quad (1)$$

where ^{X}Ar denotes the total atmospheric abundance, $N_X(t)$ is the rate of addition of isotope X to the atmosphere due to planetary degassing and meteorite accretion, $P(t)$ is atmospheric pressure, and $L(t)$ is the rate of atmospheric pressure loss due to impact erosion. The latter are related by:

$$\frac{dP}{dt} = I(t) - L(t), \quad (2)$$

where $I(t)$ is the total rate of atmospheric pressure increase due to planetary degassing of all gaseous species, which is essentially equal to the rate of increase in CO_2 since it comprises >95% of the present atmosphere.

To constrain the initial martian atmospheric pressure and its subsequent evolution, we simulated a range of hypothetical paleoatmospheric pressure paths. In each scenario, $P(t)$ declines over time due to impact erosion of atmospheric gases (i.e., L remains greater than I). We assume that other escape processes that enrich ^{40}Ar relative to ^{36}Ar (i.e., pick-up ion sputtering and hydrodynamic escape) were not significant during the first 400 million years of the Noachian due to the existence of a magnetic dynamo (Cassata et al., 2010; Brain and Jakosky, 1998; Hutchins et al., 1997; Roberts et al., 2009; Weiss et al., 2008). Only minor differences in the inferred atmospheric pressures would results if such processes were included in our model (discussed below). We allow for initial atmospheric pressures between 0.1 and 10 bar, and then explore various scenarios in which pressure declines either randomly, exponentially with the same scale parameter as that of the martian impact flux (Melosh and Vickery, 1989) (to approximate impact erosion in absence of planetary degassing), or linearly to final pressures of 0.01–1 bar at 4.16 Ga (to approximate an exponential rate of loss due to impact erosion damped by increases in pressure due to planetary degassing). Using these $P(t)$ curves and a planetary degassing model (discussed below), we then solved Eqs. (1) and (2) to constrain paleoatmospheric pressure paths that yield $^{40}Ar/^{36}Ar$ ratios of 626 ± 100 at 4.16 Ga. A detailed description of our implementation of Eqs. (1) and (2) is given in the Supplementary Files.

3. Model parameters

To calculate the production of atmospheric volatiles associated with surface, crustal, and upper mantle magmatic activity, we adopted the crustal growth model of Breuer and Spohn (2006) for an initial mantle temperature of 2000 K and no primordial crust (a summary of all model parameters is given in Table 1). Relative to other models, Breuer and Spohn (2006) predict a higher rate of magma production and, therefore, ^{40}Ar delivery to the atmosphere. Because a higher ^{40}Ar production rate demands higher atmospheric pressure (i.e., more atmospheric ^{36}Ar) to maintain a given $^{40}Ar/^{36}Ar$ ratio, using Breuer and Spohn (2006) places an upper bound on permissible atmospheric pressures during the Noachian. Less voluminous magmatic production models would predict up to an order of magnitude lower pressures during the Noachian. We assumed that magmas contain between 1300 ppm K (e.g., Nakhla meteorite; Dreibus et al., 1982) and 3300 ppm K (e.g., Mars' crust; Taylor et al., 2006). To estimate the concentration of CO_2 in magmas we used values published for melt inclusions in martian meteorites, which typically range from 5 to 500 ppm (Boctor et al., 2005). This is consistent with estimates of magmatic CO_2 concentrations based on thermodynamic equilibrium between dissolved carbon and graphite in the martian mantle (50–500 ppm; Hirschmann and Withers, 2008), and measurements of CO_2 concentrations in MORB source regions (<250 ppm; Saal et al., 2002). No direct measurements of ^{36}Ar concentrations in martian meteorite melt inclusions have been published. We assumed that the $^{36}Ar/CO_2$ ratio observed in ALH 84001 pyroxenes (~10^{-8}–10^{-9}; Cassata et al., 2010; Boctor et al., 2006). reflects that of mantle melts.[1] The model results differ by less than approximately a factor of two over the ranges in assumed magmatic K, ^{36}Ar, and CO_2 concentrations (see Supplementary Files).

To model the mass of ^{40}Ar added to the atmosphere by asteroids, we used the martian impact flux derived by Melosh and Vickery (1989) from the lunar cratering record of Neukum and Wise (1976) following Manning et al. (2006) (see Supplementary Files). We assumed that impacting asteroids contain a chondritic abun-

[1] $^{36}Ar/CO_2$ ratio for ALH 84001 orthopyroxene based on 14–167 ppm CO_2 (Boctor et al., 2006) and 0.3 ppt ^{36}Ar (excludes cosmogenic ^{36}Ar; Cassata et al., 2010).

Table 1
Definitions of model parameters and their values.

Parameter	Notation	Parameter range[a]	Preferred value	Unit	Ref.
Radius of Mars	r		3400×10^3	m	1
Mass of bulk sililcate Mars (BSM)[b]	m_{BSM}		5.11×10^{23}	kg	2
Surface gravity	g		1700×10^3	m/s^2	1
K concentration in magmas	$[K]_{magma}$	1300–3300	2500	ppm	3, 4
K concentration in impactors	$[K]_{impact}$		550	ppm	5
^{36}Ar concentration in impactors	$[^{36}Ar]_{impact}$		15	ppt	6
($N_2 + CO_2$) concentration in magmas	$[CN]_{magma}$	5–500	250	ppm	7, 8, 9
Magmatic $^{36}Ar/(N_2 + CO_2)$ ratio	R_{magma}	10^{-8}–10^{-9}	5×10^{-9}		10, 11
Initial atmospheric $^{36}Ar/(N_2 + CO_2)$ ratio	R_{atm}	10^{-4}–10^{-6}	10^{-5}		
Magma flux[c]	$V_{magma}(t)$		Breuer and Spohn (2006)	kg/Ma	12
Magma density	ρ_{magma}		3000	kg/km^3	
Impactor flux[d]	$V_{impact}(t)$		Melosh and Vickery (1989)	kg/Ma	13, 14

1: Sohl and Spohn (1997); 2: Lodders and Fegley (1997); 3: Dreibus et al. (1982); 4: Taylor et al. (2006); 5: McDonough and Sun (1995); 6: Zahringer (1966); 7: Saal et al. (2002); 8: Boctor et al. (2005); 9: Hirschmann and Withers (2008); 10: Cassata et al. (2010); 11: Boctor et al. (2006); 12: Breuer and Spohn (2006); 13: Melosh and Vickery (1989); 14: Neukum and Wise (1976).
[a] See text for details and Supplementary Files for an analysis of the model sensitivity to the parameter range.
[b] Calculated assuming the martian core is 20 wt.% and BSM is 80 wt.%.
[c] Breuer and Spohn (2006) is the crustal production model of Breuer and Spohn (2006) (see text for details).
[d] Melosh and Vickery (1989) is the martian impact flux derived by Melosh and Vickery (1989) (see text for details).

dance of K (550 ppm; McDonough and Sun, 1995) and ^{36}Ar concentrations typical of H-, L-, and LL-chondrites (∼15 ppt; Zahringer, 1966). Impact-derived ^{40}Ar is negligible in comparison to mantle-derived ^{40}Ar (<1%). We neglect the insignificant amounts of CO_2 and N_2 brought to Mars by impactors.

3.1. The initial atmospheric $^{36}Ar/(N_2{+}CO_2)$ ratio

The extent to which the addition of ^{40}Ar increases the atmospheric $^{40}Ar/^{36}Ar$ ratio is inversely proportional to the abundance of atmospheric ^{36}Ar. Thus, an important variable in our model is the primordial abundance of atmospheric ^{36}Ar, which, in an atmosphere composed primarily of N_2 and CO_2 can be expressed as initial atmospheric pressure (P_o) multiplied by the initial atmospheric $^{36}Ar/(N_2 + CO_2)$ ratio. The current martian atmospheric $^{36}Ar/(CO_2 + N_2)$ ratio is $\sim 10^{-5}$ (Bogard et al., 2001; Owen et al., 1977)[2], but this ratio may have been different in the past as atmospheric escape processes, mantle degassing, and authigenic mineralization of carbonates have fractionated N_2, CO_2, and Ar over time. To determine maximum atmospheric pressures during the Noachian we must estimate the minimum primordial $^{36}Ar/(CO_2 + N_2)$ ratio; the lowest value *a priori* implies the greatest abundance of atmospheric CO_2 and N_2 for a given quantity of ^{36}Ar. We will ultimately assume an initial atmospheric $^{36}Ar/(CO_2 + N_2)$ ratio of 10^{-5} for reasons discussed below.

Authigenic mineralization of carbonates enriches the relative concentration of atmospheric Ar by depleting CO_2. While spectral observations have not identified massive near-surface carbonate deposits (Bandfield, 2002; Bibring et al., 2006), carbonate has been discovered in outcrops in the Nili Fossae region (Michalski and Niles, 2010) and the Columbia Hills of Gusev crater (Morris et al., 2010; Christensen et al., 2004), in regolith at the Phoenix landing site (Boynton et al., 2009), and in some martian meteorites (e.g., ALH 84001). We can estimate the extent to which CO_2 has been depleted relative to other atmospheric gases by comparing Mars' volatile budget with that of other terrestrial planets (Owen and Bar-Nun, 1995). The atmospheres of Venus and Earth have similar C/N ratios of ∼15 (Donahue and Pollack, 1983) and 20 ± 10 (Owen and Bar-Nun, 1995), respectively, when CO_2 bound in carbonates is considered in the terrestrial inventory. The similarity of these planetary volatile ratios presumably reflects derivation from common meteoritic sources that were also parental to the martian atmosphere (Anders and Owen, 1977). Mars' atmospheric C/N ratio is not directly comparable to that of Earth and Venus because non-thermal escape processes have fractionated C and N over time. Based on Mars' heavy $^{15}N/^{14}N$ ratio (Jakosky and Phillips, 2001), these processes are estimated to have removed approximately 90% of Mars' atmospheric N not lost to space via impact erosion (Jakosky and Phillips, 2001). Assuming no loss of atmospheric CO_2 (as a limiting constraint to place an upper bound on CO_2 that might be contained in carbonates), the fractionation-corrected martian atmospheric C/N ratio is ∼2. If we assume that the difference between this ratio and that of Earth and Venus (∼15) reflects CO_2 bound in carbonates, then CO_2 has been depleted by up to ∼87% (i.e., 13/15) relative to N. Similarly, Owen and Bar-Nun (1995) estimated that CO_2 has been depleted by 90% relative to Kr based on differences between the martian atmospheric ^{84}Kr/C ratio and that of Earth and Venus. The mass of near-surface carbonates associated with this CO_2 depletion depends on atmospheric pressures at times when deposition occurred.

[2] Calculated assuming the martian atmosphere contains 1.6% Ar by volume (Owen et al., 1977) with a 40Ar/36Ar ratio of 1800 (Bogard et al., 2001).

The effect of the abovementioned CO_2 sequestration on the atmospheric $^{36}Ar/(CO_2 + N_2)$ would be offset, at least in part, by the preferential atmospheric escape of Ar relative to CO_2, and by mantle degassing. Based on Mars' elevated $^{38}Ar/^{36}Ar$ ratio of ∼0.24 (Bogard et al., 2001), non-thermal escape processes are estimated to have removed approximately 50% of Mars' atmospheric Ar not lost to space via impact erosion (Jakosky and Phillips, 2001). If we assume no loss of atmospheric CO_2 (to be consistent with the constraints on CO_2 sequestration imposed above), then CO_2 has then been enriched by up to 50% relative to ^{36}Ar. Likewise, planetary degassing enriches the atmosphere in CO_2 as mantle-derived volatiles are depleted in ^{36}Ar relative to the atmosphere (discussed above). In our model, ∼2 bars of mantle-derived CO_2 are degassed; the resulting enrichment in CO_2 relative to ^{36}Ar is directly proportional to atmospheric pressure, and is >25% at initial atmospheric pressures as high as 5 bars. Altogether, we expect that increases in the atmospheric $^{36}Ar/(CO_2 + N_2)$ ratio due to CO_2 sequestration in carbonates (up to 90%) were approximately offset by decreases due to escape processes (up to 50%) and mantle degassing (>25%). Thus we use a primordial atmospheric $^{36}Ar/(CO_2 + N_2)$ ratio of 10^{-5} in our preferred model, with one log unit uncertainty. Fractionation of N_2 has been ignored because of its low abundance relative to CO_2.

4. Results and discussion

In Fig. 2, using our preferred model parameters (Table 1), we show a selection of linearly and exponentially decreasing paleoatmospheric pressure paths that yield an $^{40}Ar/^{36}Ar$ ratio of 626 ± 100 at 4.16 Ga. A more extensive array of pressure paths that succeed and fail to predict this ratio, along with an analysis of the model sensitivities to each of four variable parameters listed in Table 1, is given in the Supplementary Files. We find that low atmospheric pressures throughout the Noachian (<1 bar on average) are required to produce the observed $^{40}Ar/^{36}Ar$ ratio at 4.16 Ga. Higher atmospheric pressures, and therefore greater *total* abundances of atmospheric ^{36}Ar, preclude an adequate increase in the $^{40}Ar/^{36}Ar$ ratio for the range in mantle degassing scenarios explored and our best estimates of planetary and atmospheric element abundances. All scenarios require atmospheric pressures of <400 mbar by 4.16 Ga, which implies up to 3.5 bars of atmospheric CO_2 were lost during the first 400 million years of the Noachian (∼2 bars of magmatic CO_2 degassed from the mantle through time plus up to 1.5 bars of the initial atmospheric CO_2).

In our model, we assume that the decline in atmospheric pressure is caused solely by impact erosion, which does not fractionate isotopes or chemical species. If, however, CO_2 sequestration into carbonates also drove down atmospheric pressures, then we have overstated the loss of ^{36}Ar by impact erosion and even lower atmospheric pressures are required to predict the $^{40}Ar/^{36}Ar$ ratio of 626 ± 100 at 4.16 Ga. Conversely, if early hydrodynamic escape preferentially removed ^{36}Ar relative to ^{40}Ar, then we have understated the loss of ^{36}Ar by impact erosion and greater atmospheric pressures are required. However, nitrogen isotopes in ALH 84001 maskelynite are significantly less fractionated than those in the modern martian atmosphere (Bogard et al., 2001), which suggests that non-thermal escape occurring throughout the past ∼4 Ga, not early hydrodynamic escape, may be principally responsible for heavy isotope enrichments. Therefore, because the modern martian atmospheric $^{38}Ar/^{36}Ar$ ratio is only enriched by 30% relative to the primordial value (Jakosky and Phillips, 2001), our model results would not differ significantly if early hydrodynamic escape were considered. Moreover, if a less voluminous magma production model than Breuer and Spohn (2006) was used, then even lower atmospheric pressures would be required (discussed above).

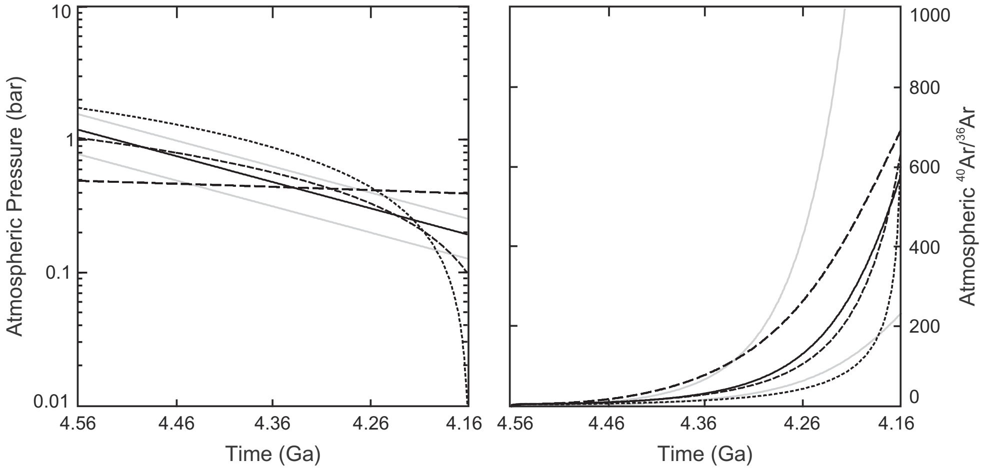

Fig. 2. Modeled paleoatmospheric pressure paths (left) and corresponding evolution in the atmospheric $^{40}Ar/^{36}Ar$ ratio (right) for the model parameters listed in Table 1. Dashed curves denote a constant rate of pressure change and solid lines an exponential decrease. Four atmospheric pressure models that predict an $^{40}Ar/^{36}Ar$ ratio within 626 ± 100 at 4.16 Ga are shown in black. For comparison, two models that fail to predict this ratio are shown in gray; an array of additional scenarios excluded by the ALH 84001 data is shown in the Supplementary Files. Linearly decreasing pressure paths were forced to evolve to pressures ranging between 10 mbar and 10 bar at 4.16 Ga; those forced to final pressures >400 mbar predict $^{40}Ar/^{36}Ar$ ratios less than 626 ± 100 and are therefore excluded. For clarity, only results for final pressures of 10 mbar, 100 mbar, and 400 mbar are shown. Exponential pressure models decline at the same rate as the martian impact flux (Melosh and Vickery, 1989) (see Supplementary Files), with ~16% of the initial pressures at 4.16 Ga. The curves shown in black are representative of the range of permissible linear, exponential, and random solutions (see Fig. S1) and require <1 bar of atmospheric pressure (on average) throughout most of the Noachian. A detailed analysis of the model sensitivity to input parameters is given in the Supplementary Files.

In summary, our model results indicate that atmospheric pressures during the Early to Middle Noachian were likely less than ~1 bar. This suggests that a long-lived, CO_2-based greenhouse atmosphere with surface temperatures above the melting point of H_2O did not exist at that time. The apparent absence of massive carbonate deposits may be consistent with this result. The model results are also consistent with the observation that the formation of phyllosilicates observed in the Noachian crust required low partial pressures of atmospheric CO_2 (Chevrier et al., 2007). Although it is possible that an extended greenhouse climate may have existed after the period of our meteoritic constraint (i.e., after 4.16 Ga), geomorphic and spectral observations indicate that the Noachian was on average the warmest and wettest period on Mars (Bibring et al., 2006; Carr and Head, 2010). Therefore, if the trapped $^{40}Ar/^{36}Ar$ ratio observed in ALH 84001 is a sample of the Noachian martian atmosphere, then even during this putative warm period it appears that water was only intermittently stable in the liquid phase.

Impact events or intense volcanism may have caused such intermittent conditions by delivering other greenhouse gases to the atmosphere, such as SO_2, H_2S, and water vapor (Toon et al., 2010). Given the partial pressures of CO_2 permitted by our model results, temporarily elevated partial pressures of these other atmospheric gases (e.g., $\sim 2 \times 10^{-6}$ bars of SO_2) could have stabilized liquid water on Mars' surface at high latitudes (Halevy et al., 2007; Johnson et al., 2008; Tian et al., 2010). The discovery of sulfate deposits in the martian regolith underscores the potential role of SO_2 and H_2S as greenhouse gases. Even in the absence of such gases, liquid water would be stable at low latitudes during seasonally warm periods given the partial pressures of CO_2 permitted by our model results. Thus, existing observations of surface and meteorite mineralogy, coupled with the trapped Ar component identified in ALH 84001, suggest that the mean Noachian climate on Mars was cool (below freezing) and dry (without liquid water), with only intermittent periods of warm and wet conditions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.icarus.2012.05.005.

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