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

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A B S T R A C T

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 substantially higher partial pressures of CO2 required to explain the alteration of Noachian surface rocks to clay minerals (~0.001–0.01 bar; Chevrier et al., 2007) rather than the low latitudes during seasonally warm periods. Other greenhouse gases like SO2 and water vapor may have played an important role in intermittently stabilizing liquid water at higher latitudes following major volcanic eruptions or impact events.

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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 CO2) 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., 10–103 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 Looey, 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-SO2 aqueous environments) and the apparently low partial pressures of CO2 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 CO2-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 SO2 and H2S may have contributed to greenhouse warming. Modest influxes of SO2 and H2S (e.g., ~2 × 10–4 bar) in the presence of only 50 mbar CO2 can promote transient periods of wet, warm conditions (Halsey et al., 2007; Johnson et al., 2008). Despite these observations, whether a dense, CO2-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 40Ar/36Ar 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 40Ar/36Ar vs. 36Ar/38Ar 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 40Ar evolution model

A comparison of the atmospheric 40Ar/36Ar 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 40Ar/36Ar ratio from its primordial ratio of ~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 40Ar/36Ar ratio increased from ~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 40Ar/36Ar ratio to more than twice the modern ratio on Earth, but only about ~1/10 the duration (~400 Ma). The relatively rapid evolution in the martian atmospheric 40Ar/36Ar ratio suggests that one or more of the following is true:

- Marti
Fig. 1. Left: 40Ar/36Ar isochron diagram for maskelynite in ALH 84001-1 [redrafted from Cassata et al. (2010)]. Correlation between the isotope ratios 39Ar/36Ar and 40Ar/36Ar 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 2σ 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 39Ar/36Ar ratio of the trapped component in ALH 84001 maskelynite is 626 ± 100. Right: Plot of the 39Ar/36Ar 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 39Ar/36Ar ratio represents the weighted average of MIL 03346 and Nakhlite meteorites (see Supplementary Files). Earth’s atmospheric 39Ar/36Ar ratio is shown for comparison. Dashed lines linearly connect data points and do not represent the evolution of the atmospheric 39Ar/36Ar 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 39Ar/36Ar 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 40Ar was generated early on Mars,

(2) the 36Ar concentration of Mars’ interior is lower than Earth’s, such that extracted magmas had elevated 40Ar/36Ar 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 40Ar was delivered from the asthenosphere to the atmosphere, and/or

(4) Mars had a thinner atmosphere than Earth (i.e., less atmospheric 36Ar), such that a given quantity of degassed 36Ar more efficiently elevated the atmospheric 39Ar/40Ar ratio.

In this paper, we use published constraints on (1)–(3) to assess whether or not (4) is a viable explanation for Mars’ elevated 39Ar/40Ar 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 39Ar/40Ar 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 39Ar/40Ar 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 40Ar/36Ar = 10 ± 3 (Begemann et al., 1976).

(2) Planetary degassing and meteorite accretion added both radiogenic volatiles (40Ar) and non-radiogenic volatiles (36Ar, N2, and CO2) to the atmosphere.

(3) Atmospheric loss due to impact erosion removed volatiles, but did not fractionate 39Ar and 40Ar (Brain and Jakosky, 1998; Melosh and Vickery, 1989).

(4) At 4.16 ± 0.04 Ga the atmospheric 39Ar/40Ar 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:

\[ \frac{dN_X}{dt} - \frac{N_X(t)}{\tau} = \frac{A_X}{(t)} \left( N(t) - L(t) \right) \]

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

\[ \frac{dP}{dt} = -\frac{A_X}{(t)} - L(t). \]

where \( L(t) \) 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 CO2 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 \( t \)). We assume that other escape processes that enrich 40Ar relative to 36Ar (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 result 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 39Ar/40Ar 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, 40Ar delivery to the atmosphere. Because a higher 40Ar production rate demands higher atmospheric pressure (i.e., more atmospheric 39Ar) to maintain a given 39Ar/40Ar 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., Nakhl meteorite; Dreibus et al., 1982) and 3300 ppm K (e.g., Mars’ crust; Taylor et al., 2006). To estimate the concentration of CO2 in magmas we used values published for melt inclusions in martian meteorites, which typically range from 5 to 500 ppm (Boctor et al., 2006). This is consistent with estimates of magmatic CO2 concentrations based on thermodynamic equilibrium between dissolved carbon and graphite in the martian mantle (50–500 ppm; Hirschmann and Withers, 2008), and measurements of CO2 concentrations in MORB source regions (<250 ppm; Saa et al., 2002). No direct measurements of 39Ar concentrations in martian meteorite melt inclusions have been published. We assumed that the 39Ar/CO2 ratio observed in ALH 84001 pyroxenes (~10–10–5; 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, 36Ar, and CO2 concentrations (see Supplementary Files).

To model the mass of 40Ar added to the atmosphere by asteroids, we used the martian impact flux derived by Melosh and Vickery (1989) from the lunar cratering model of Neukum and Wies (1976) following Manning et al. (2006) (see Supplementary Files). We assumed that impacting asteroids contain a chondritic abundance...
The effect of the abovementioned CO2 sequestration on the atmospheric 40Ar/36Ar (CO2 + N2) would be offset, at least in part, by the preferential atmospheric escape of Ar relative to CO2, and by mantle degassing. Based on Mars' elevated 40Ar/36Ar 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 a loss of atmospheric CO2 (to be consistent with the constraints on CO2 sequestration imposed above), then CO2 has then been enriched by up to 50% relative to Ar. Likewise, planetary degassing enriches the atmosphere in CO2 as mantle-derived volatiles are depleted in 40Ar relative to the atmosphere (discussed above). In our model, -2 bars of mantle-derived CO2 are degassed; the resulting enrichment in CO2 relative to 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 40Ar/36Ar ratio due to CO2 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 40Ar/36Ar ratio of 10^{-6} in our preferred model, with one log unit uncertainty. Fractionation of N2 has been ignored because of its low abundance relative to CO2.

4. Results and discussion

In Fig. 2, using our preferred model parameters (Table 1), we show a selection of linearly and exponentially decreasing palaeoatmospheric pressure paths that yield an 40Ar/36Ar 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 40Ar/36Ar ratio at 4.16 Ga. Higher atmospheric pressures, and therefore greater total abundances of atmospheric Ar, preclude an adequate increase in the 40Ar/36Ar 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 CO2 were lost during the first 400 million years of the Noachian (~2 bars of magmatic CO2 degassed from the mantle through time plus up to 1.5 bars of the initial atmospheric CO2).

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, CO2 sequestration into carbonates also drove down atmospheric pressures, then we have overstated the loss of 36Ar by impact erosion and even lower atmospheric pressures are required to predict the 36Ar/40Ar ratio of 626 ± 100 at 4.16 Ga. Conversely, if early hydrodynamic escape preferentially removed 36Ar relative to Ar, then we have understated the loss of 36Ar by impact erosion and even lower 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 occurred throughout the past ~4 Ga, not early hydrodynamic escape. Therefore, because the modern martian atmospheric 36Ar/40Ar 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 was considered. Moreover, if a less voluminous magma reservoir model than Breuer and Spohn (2006) was used, even lower atmospheric pressures would be required (discussed above).

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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).

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Table 1
Definitions of model parameters and their values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Notation</th>
<th>Parameter range</th>
<th>Preferred value</th>
<th>Unit</th>
<th>Ref.</th>
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<td>3400 x 10^{-11}</td>
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<td>Mass of bulk silicate Mars (BSM)</td>
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<td>ppm</td>
<td>3, 4</td>
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<tr>
<td>K concentration in impactors</td>
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<td>6</td>
<td></td>
<td></td>
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<tr>
<td>36Ar concentration in impactors</td>
<td>[36Ar]_{impact}</td>
<td>15</td>
<td></td>
<td>ppt</td>
<td></td>
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<td>40Ar/36Ar concentration in magmas</td>
<td>[CN]_{magmas}</td>
<td>5–500</td>
<td>2500</td>
<td>ppm</td>
<td>7, 8, 9</td>
</tr>
<tr>
<td>Magmatic 36Ar/(N2 + CO2) ratio</td>
<td>R_{mag}</td>
<td>10^{-6}–10^{-9}</td>
<td>5 x 10^{-9}</td>
<td></td>
<td>10, 11</td>
</tr>
<tr>
<td>Initial atmospheric 36Ar/(N2 + CO2)</td>
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<td>10^{-5}</td>
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<td></td>
<td></td>
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<td>Breuer and Spohn (2006)</td>
<td>kg/Ma</td>
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<tr>
<td>Magma density</td>
<td>d_{magma}</td>
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<td>Breuer and Spohn (2006)</td>
<td>kg/km^3</td>
<td>13, 14</td>
</tr>
<tr>
<td>Impactor flux</td>
<td>f_{impact}</td>
<td>3000</td>
<td>Melosh and Vickery (1989)</td>
<td>kg/Ma</td>
<td>13, 14</td>
</tr>
</tbody>
</table>

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1: Sohl and Spohn (1997); 2: Lodders and Fegley (1997); 3: Dredhuis et al. (1982); 4: Taylor et al. (2006); 5: McDonough and Sun (1995); 6: Zahniser (1986); 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).

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6 See text for details and Supplementary Files for an analysis of the model sensitivity to the parameter range.
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, CO₂-based greenhouse atmosphere with surface temperatures above the melting point of H₂O 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 CO₂ (Chevrier et al., 2007). Although it is possible that an extended greenhouse climate may have existed after the period of our meteoric 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 ⁴⁰Ar/³⁶Ar 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 SO₂, H₂S, and water vapor (Toon et al., 2010). Given the partial pressures of CO₂ permitted by our model results, temporarily elevated partial pressures of these other atmospheric gases (e.g., ~2 × 10⁻⁶ bars of SO₂) 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 SO₂ and H₂S 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 CO₂ 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.

Fig. 2. Modeled paleoatmospheric pressure paths (left) and corresponding evolution in the atmospheric ⁴⁰Ar/³⁶Ar 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 ⁴⁰Ar/³⁶Ar 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 ⁴⁰Ar/³⁶Ar 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.