1		
2		
3		
4		
5		
6	Tra	apped Ar isotopes in meteorite ALH 84001 indicate Mars did not have a thick ancient atmosphere
7		
8		William S. Cassata <sup>1,2,*</sup> , David L. Shuster <sup>1,2</sup> , Paul R. Renne <sup>1,2</sup> , Benjamin P. Weiss <sup>3</sup>
9		
10	1.	Department of Earth and Planetary Science, University of California - Berkeley, 307 McCone Hall #4767,
11		Berkeley, CA 94720-4767, USA (cassata@berkeley.edu)
12	2.	Berkeley Geochronology Center, 2455 Ridge Road, Berkeley, CA 94709, USA (prenne@bgc.org,
13		dshuster@bgc.org)
14	3.	Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 77
15		Massachusetts Avenue, Cambridge, MA 02139, USA (bpweiss@mit.edu)
16		
17	*	Corresponding author
18		
19		
20		
21		
22		
23		
24		
25		
26		
27		

28 Water is not currently stable in liquid form on the Martian surface due to the present mean atmospheric 29 pressure of ~7 mbar and mean global temperature of ~220 K. However, geomorphic features and hydrated 30 mineral assemblages suggest that Mars' climate was once warmer and liquid water flowed on the surface. 31 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 <sup>40</sup>Ar/<sup>36</sup>Ar ratios of 32 33 trapped gases within Martian meteorite ALH 84001 constrain paleoatmospheric pressure on Mars during the 34 Noachian Era [~4.56-3.8 billion years (Ga)]. Our model indicates that atmospheric pressures did not exceed 35 ~1.5 bar during the first 400 million years (Ma) of the Noachian era, and were <400 mbar by 4.16 Ga. Such 36 pressures of CO<sub>2</sub> are only sufficient to stabilize liquid water on Mars' surface at low latitudes during 37 seasonally warm periods. Other greenhouse gases like SO<sub>2</sub> and water vapor may have played an important 38 role in intermittently stabilizing liquid water at higher latitudes following major volcanic eruptions or impact 39 events.

40 The composition and mass of the ancient Martian atmosphere are key parameters of planetary evolution that 41 remain poorly understood. Radiative transfer models suggest that a greater pressures of greenhouse gases in the past 42 (e.g., >5 bars of CO<sub>2</sub>) were necessary to sustain surface temperatures above freezing for prolonged durations<sup>1-5</sup>. 43 Alternatively, large impacts may have vaporized subsurface volatiles and generated relatively brief periods of warm 44 and wet conditions (e.g.,  $10^2$ - $10^3$  years)<sup>6</sup>, which may explain why a decrease in fluvial erosion appears to coincide 45 with the end of the heavy impact bombardment<sup>7</sup>. Both explanations imply climate conditions during the Noachian 46 era that were significantly different from the present. However, whereas prolonged periods of high concentrations 47 of greenhouse gases implicate warm and wet surface environments conducive to life, intermittent impact-driven 48 greenhouse events do not.

Observational constraints on past climate conditions on Mars are limited. The scarcity of carbonate minerals<sup>8-10</sup> (expected to form in low-SO<sub>2</sub> aqueous environments) and the apparently low partial pressures of CO<sub>2</sub> required to explain the alteration of Noachian surface rocks to clay minerals  $(0.001-0.01 \text{ bar})^{11}$  suggest that a dense CO<sub>2</sub>-rich atmosphere did not persist throughout the Noachian. The identification of sulfate deposits in the Martian regolith<sup>12-14</sup> indicates that atmospheric SO<sub>2</sub> and H<sub>2</sub>S may have contributed to greenhouse warming. Modest influxes of SO<sub>2</sub> and H<sub>2</sub>S (e.g.,  $\sim 2 \times 10^{-6}$  bar) in the presence of only 50 mbar CO<sub>2</sub> can promote transient periods of warm, wet conditions<sup>15,16</sup>. Despite these observations, whether a dense, CO<sub>2</sub>-rich atmosphere ever existed and the extent to

2

56 which other greenhouse gases contributed to warming remain poorly understood.

57 Martian meteorites contain trapped atmospheric gases<sup>17</sup> that provide chemical constraints on past atmospheric conditions. Cassata et al.<sup>18</sup> identified a trapped argon (Ar) component within maskelynite in the  $4.16 \pm 0.04$  Ga old 58 59 Martian meteorite ALH 84001 with an  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio of 626 ± 100 (Fig. 1). Here we present the first attempt to use 60 this isotopic composition to constrain atmospheric pressure on Mars between the time of planetary formation and the 61 4.16 Ga age of the maskelynite. We discuss the implications of these pressure limits for greenhouse warming, 62 atmospheric evolution, and climate on Mars during the Noachian era. Critical to our arguments is the assumption 63 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 64 65 strong support for such an interpretation; terrestrial feldspars and glasses with appreciably non-atmospheric trapped 66 components generally fail to produce linear isochron diagrams (discussed in detail in the supplementary files).

67

#### 68 An atmospheric <sup>40</sup>Ar evolution model

69 A comparison of the atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratios of Earth and Mars reveals significant differences in the 70 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  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratio from its primordial ratio of ~10<sup>-3</sup> at 4.56 71  $Ga^{19}$  to the present value of >298<sup>20</sup>. Meteorite measurements indicate that on Mars, the atmospheric  ${}^{40}Ar/{}^{36}Ar$  ratio 72 increased from ~10<sup>-3</sup> at 4.56 Ga, to  $626 \pm 100$  at 4.16 Ga, to the present value of ~1800<sup>17</sup>. Thus, the net effects of 73 74 Martian planetary degassing and late stage planetary accretion increased the Martian atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio to 75 more than twice the modern ratio on Earth, but over only  $\sim 1/10$  the duration ( $\sim 400$  Ma). The relatively rapid evolution in the Martian atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio suggests that one or more of the following is true: 76 77 (1) the potassium (K) concentration of Mars is greater than Earth, such that significantly more radiogenic <sup>40</sup>Ar 78 was generated early on Mars, 79 (2) the <sup>36</sup>Ar concentration of Mars' interior is lower than Earth's, such that extracted magmas had elevated <sup>40</sup>Ar/<sup>36</sup>Ar ratios relative to terrestrial magmas of equivalent age and K concentration, 80 81 (3) planetary degassing was more efficient on early Mars than Earth, such that a greater proportion of

82 radiogenic <sup>40</sup>Ar was delivered from the astheno-lithosphere to the atmosphere, and/or

- 83 (4) Mars had a thinner atmosphere than Earth (i.e., less atmospheric  $^{36}$ Ar), such that a given quantity of
- 84

degassed  ${}^{40}$ Ar more efficiently elevated the atmospheric  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio.

85 In this paper, we use published constraints on (1) - (3) to assess whether or not (4) is a viable explanation for Mars' elevated <sup>40</sup>Ar/<sup>36</sup>Ar ratio at 4.16 Ga. We simulate planetary degassing under a broad range of atmospheric 86 87 pressure conditions and explore the resulting evolution in the Martian atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio during the 88 Noachian. Our objective is to place bounds on atmospheric pressures during the first ~400 Ma of Martian history 89 that are consistent with an  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratio of  $626 \pm 100$  at 4.16 Ga. We begin with the following postulates: (1) Mars was assembled from bodies that had an initial inventory of volatiles with  ${}^{40}\text{Ar}/{}^{36}\text{Ar} < 10^{-3}$  (ref. <sup>19</sup>). 90 (2) Planetary degassing and meteorite accretion added both radiogenic volatiles (<sup>40</sup>Ar) and non-radiogenic 91 92 volatiles ( $^{36}$ Ar, N<sub>2</sub>, and CO<sub>2</sub>) to the atmosphere. (3) Atmospheric loss due to impact erosion removed volatiles, but did not fractionate  ${}^{36}$ Ar and  ${}^{40}$ Ar ${}^{21,22}$ . 93

94 (4) At  $4.16 \pm 0.04$  Ga the atmospheric  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio was  $626 \pm 100$ , as indicated by the trapped component in 95 ALH 84001 maskelynite<sup>18</sup>.

96 Under these conditions, the atmospheric molar abundance of Ar isotope *X* varies through time according to the97 following equation:

98 
$$\frac{d^{X}Ar}{dt} = N_{X}\left(t\right) - \left({}^{X}Ar\frac{L(t)}{P(t)}\right),$$
(1)

where <sup>*X*</sup>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:

$$102 \qquad \frac{dP}{dt} = I(t) - L(t), \tag{2}$$

103 where I(t) is the total rate of atmospheric pressure increase due to planetary degassing of all gaseous species,

- 104 which is essentially equal to the rate of increase in  $CO_2$  since it comprises >95% of the present atmosphere.
- 105 To constrain the initial Martian atmospheric pressure and its subsequent evolution, we simulated a range of
- 106 hypothetical paleoatmospheric pressure paths. In each scenario, P(t) declines over time due to impact erosion of
- 107 atmospheric gases (i.e., L remains greater than I). We assume that other escape processes that enrich <sup>40</sup>Ar relative to
- <sup>36</sup>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<sup>18,21,23-25</sup>. Only minor differences in the inferred atmospheric
 pressures would results if such processes were included in our model (discussed below). We allow for initial

- 111 atmospheric pressures between 0.1 and 10 bar, and then explore various scenarios in which pressure declines either
- 112 randomly, exponentially with the same scale parameter as that of the Martian impact flux<sup>22</sup> (to approximate impact
- erosion in absence of planetary degassing), or linearly to final pressures of 0.01 to 1 bar at 4.16 Ga (to approximate
- 114 an exponential rate of loss due to impact erosion damped by increases in pressure due to planetary degassing). Using
- 115 these *P*(*t*) curves and a planetary degassing model (discussed below), we then solved Eqs. (1) and (2) to constrain
- 116 paleoatmospheric pressure paths that yield  ${}^{40}$ Ar/ ${}^{36}$ Ar ratios of 626 ± 100 at 4.16 Ga. A detailed description of our
- 117 implementation of equations (1) and (2) is given in the supplementary files.
- 118

#### 119 Model Parameters

120 To calculate the production of atmospheric volatiles associated with surface, crustal, and upper mantle 121 magmatic activity, we adopted the crustal growth model of Breuer and Spohn<sup>26</sup> for an initial mantle temperature of 122 2000 K and no primordial crust (a summary of all model parameters is given in Table 1). Relative to other models, 123 Breuer and Spohn<sup>26</sup> predict a higher rate of magma production and, therefore, <sup>40</sup>Ar delivery to the atmosphere. 124 Because a higher <sup>40</sup>Ar production rate demands higher atmospheric pressure (i.e., more atmospheric <sup>36</sup>Ar) to 125 maintain a given  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio, using Breuer and Spohn ${}^{26}$  places an upper bound on permissible atmospheric 126 pressures during the Noachian. Less voluminous magmatic production models would predict up to an order of 127 magnitude lower pressures during the Noachian. We assumed that magmas contain between 1300 ppm K (e.g., 128 Nakhla meteorite)<sup>27</sup> and 3300 ppm K (e.g., Mars' crust)<sup>28</sup>. To estimate the concentration of CO<sub>2</sub> in magmas we used 129 values published for melt inclusions in Martian meteorites, which typically range from  $5-500 \text{ ppm}^{29}$ . This is 130 consistent with estimates of magmatic CO<sub>2</sub> concentrations based on thermodynamic equilibrium between dissolved 131 carbon and graphite in the Martian mantle  $(50-500 \text{ ppm})^{30}$ , and measurements of CO<sub>2</sub> concentrations in MORB source regions (<250 ppm)<sup>31</sup>. No direct measurements of <sup>36</sup>Ar concentrations in Martian meteorite melt inclusions 132 have been published. We assumed that the  ${}^{36}$ Ar/CO<sub>2</sub> ratio observed in ALH 84001 pyroxenes (~10<sup>-8</sup>-10<sup>-9</sup>)<sup>18,32</sup> 133

134 reflects that of mantle melts<sup>1</sup>. The model results differ by less than approximately a factor of two for the ranges in

135 assumed magmatic K, <sup>36</sup>Ar, and CO<sub>2</sub> concentrations (see supplementary files).

136 To model the mass of <sup>40</sup>Ar added to the atmosphere by asteroids, we used the Martian impact flux derived by

137 Melosh and Vickery<sup>22</sup> from the lunar cratering record of Neukum and Wise<sup>33</sup> following Manning et al.<sup>34</sup> (see

- 138 supplementary files). We assumed that impacting asteroids contain a chondritic abundance of K (550 ppm)<sup>35</sup> and
- <sup>36</sup>Ar concentrations typical of H-, L-, and LL-chondrites (~15 ppt)<sup>36</sup>. Impact-derived <sup>40</sup>Ar is negligible in

140 comparison to mantle-derived  $^{40}$ Ar (<1%). We neglect the insignificant amounts of CO<sub>2</sub> and N<sub>2</sub> brought to Mars by 141 impactors.

142

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

144 The extent to which the addition of  ${}^{40}$ Ar increases the atmospheric  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio is inversely proportional to 145 the abundance of atmospheric  ${}^{36}$ Ar. Thus, an important variable in our model is the primordial abundance of

146 atmospheric  ${}^{36}$ Ar, which, in an atmosphere composed primarily of N<sub>2</sub> and CO<sub>2</sub>, can be expressed as initial

147 atmospheric pressure ( $P_0$ ) multiplied by the initial atmospheric <sup>36</sup>Ar/(N<sub>2</sub>+CO<sub>2</sub>) ratio. The current Martian

148 atmospheric  ${}^{36}$ Ar/(CO<sub>2</sub>+N<sub>2</sub>) ratio is ~10<sup>-5</sup> (refs. 17,37)<sup>2</sup>, but this ratio may have been different in the past as

149 atmospheric escape processes, mantle degassing, and authigenic mineralization of carbonates have fractionated N<sub>2</sub>,

150 CO<sub>2</sub>, and Ar over time. To determine maximum atmospheric pressures during the Noachian we must estimate the

151 minimum primordial  ${}^{36}$ Ar/(CO<sub>2</sub>+N<sub>2</sub>) ratio; the lowest value *a priori* implies the greatest abundance of atmospheric

152  $CO_2$  and  $N_2$  for a given quantity of <sup>36</sup>Ar. We will ultimately assume an initial atmospheric <sup>36</sup>Ar/( $CO_2+N_2$ ) ratio of

 $153 \quad 10^{-5}$  for reasons discussed below.

154 Authigenic mineralization of carbonates enriches the relative concentration of atmospheric Ar by depleting

155 CO<sub>2</sub>. While spectral observations have not identified massive near-surface carbonate deposits<sup>8,9</sup>, carbonate has been

- 156 discovered in outcrops in the Nili Fossae region<sup>38</sup> and the Columbia Hills of Gusev crater<sup>39,40</sup>, in regolith at the
- 157 Phoenix landing site<sup>41</sup>, and in some Martian meteorites (e.g., ALH 84001). We can estimate the extent to which CO<sub>2</sub>
- 158 has been depleted relative to other atmospheric gases by comparing Mars' volatile budget with that of other
- 159 terrestrial planets<sup>42</sup>. The atmospheres of Venus and Earth have similar C/N ratios of ~15 (ref. <sup>43</sup>) and  $20 \pm 10$  (ref.

 $<sup>^{1.36}</sup>$ Ar/CO<sub>2</sub> ratio for ALH 84001 orthopyroxene based on 14-167 ppm CO<sub>2</sub> (Boctor et al., 2006) and 0.3 ppt  $^{36}$ Ar (excludes cosmogenic  $^{36}$ Ar; Cassata et al., 2010).

<sup>&</sup>lt;sup>2</sup> Calculated assuming the Martian atmosphere contains 1.6% Ar by volume (Owen et al., 1977) with a  $^{40}$ Ar/ $^{36}$ Ar ratio of 1800 (Bogard et al., 2001).

160  $^{42}$ ), respectively, when CO<sub>2</sub> bound in carbonates is considered in the terrestrial inventory. The similarity of these 161 planetary volatile ratios presumably reflects derivation from common meteoritic sources that were also parental to 162 the Martian atmosphere<sup>44</sup>. Mars' atmospheric C/N ratio is not directly comparable to that of Earth and Venus 163 because non-thermal escape processes have fractionated C and N over time. Based on Mars' heavy  ${}^{15}N/{}^{14}N$  ratio<sup>1</sup>, 164 these processes are estimated to have removed approximately 90% of Mars' atmospheric N not lost to space via 165 impact erosion<sup>1</sup>. Assuming no loss of atmospheric  $CO_2$  (as a limiting constraint), the fractionation-corrected Martian 166 atmospheric C/N ratio is ~2. If we assume that the difference between this ratio and that of Earth and Venus (~15) 167 reflects CO<sub>2</sub> bound in carbonates, then CO<sub>2</sub> has been depleted by up to  $\sim 87\%$  (i.e., 13/15) relative to N. Similarly, Owen and Bar-Nun<sup>42</sup> estimated that CO<sub>2</sub> has been depleted by 90% relative to Kr based on differences between the 168 169 Martian atmospheric <sup>84</sup>Kr/C ratio and that of Earth and Venus. The mass of near-surface carbonates associated with 170 this CO<sub>2</sub> depletion depends on atmospheric pressures at times when deposition occurred. 171 The effect of the abovementioned  $CO_2$  sequestration on the atmospheric  ${}^{36}Ar/(CO_2+N_2)$  would be offset, at least 172 in part, by the preferential atmospheric escape of Ar relative to CO<sub>2</sub>, and by mantle degassing. Based on Mars' 173 elevated  ${}^{38}$ Ar/ ${}^{36}$ Ar ratio of ~0.24 $^{17}$ , non-thermal escape processes are estimated to have removed approximately 50% 174 of Mars' atmospheric Ar not lost to space via impact erosion<sup>1</sup>. If we assume no loss of atmospheric  $CO_2$  (to be 175 consistent with the constraints on  $CO_2$  sequestration imposed above), then  $CO_2$  has then been enriched by up to 50% 176 relative to <sup>36</sup>Ar. Likewise, planetary degassing enriches the atmosphere in CO<sub>2</sub> as mantle-derived volatiles are depleted in  $^{36}$ Ar relative to the atmosphere (discussed above). In our model, ~2 bars of mantle-derived CO<sub>2</sub> are 177 178 degassed; the resulting enrichment in CO<sub>2</sub> relative to <sup>36</sup>Ar is directly proportional to atmospheric pressure, and is 179 >25% at initial atmospheric pressures as high as 5 bars. Altogether, we expect that increases in the atmospheric 180  $^{36}$ Ar/(CO<sub>2</sub>+N<sub>2</sub>) ratio due to CO<sub>2</sub> sequestration in carbonates (up to 90%) were approximately offset by decreases due 181 to escape processes (up to 50%) and mantle degassing (>25%). Thus we use a primordial atmospheric 182  $^{36}$ Ar/(CO<sub>2</sub>+N<sub>2</sub>) ratio of 10<sup>-5</sup> in our preferred model, with one log unit uncertainty. Fractionation of N<sub>2</sub> has been 183 ignored because of its low abundance relative to CO<sub>2</sub>.

184

# 185 **Results and discussion**

186 In Figure 2, using our preferred model parameters (Table 1), we show a selection of linearly and exponentially 187 decreasing paleoatmospheric pressure paths that yield an  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio of 626 ± 100 at 4.16 Ga. A more extensive

188 array of pressure paths that succeed and fail to predict this ratio, along with an analysis of the model sensitivities to 189 each of four variable parameters listed in Table 1, is given in the supplementary files. We find that low atmospheric 190 pressures throughout the Noachian (<1 bar on average) are required to produce the observed  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio at 4.16 191 Ga. Higher atmospheric pressures, and therefore greater *total* abundances of atmospheric <sup>36</sup>Ar, preclude an adequate 192 increase in the <sup>40</sup>Ar/<sup>36</sup>Ar ratio for the range in mantle degassing scenarios explored and our best estimates of 193 planetary and atmospheric element abundances. All scenarios require atmospheric pressures of <400 mbar by 4.16 194 Ga, which implies up to 3.5 bars of atmospheric CO<sub>2</sub> were lost during the first 400 million years of the Noachian ( $\sim 2$ 195 bars of magmatic  $CO_2$  degassed from the mantle through time plus up to 1.5 bars of the initial atmospheric  $CO_2$ ). 196 In our model, we assume that the decline in atmospheric pressure is caused solely by impact erosion, which 197 does not fractionate isotopes or chemical species. If, however, CO<sub>2</sub> sequestration into carbonates also drove down 198 atmospheric pressures, then we have overstated the loss of <sup>36</sup>Ar by impact erosion and even lower atmospheric 199 pressures are required to predict the  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio of 626 ± 100 at 4.16 Ga. Conversely, if early hydrodynamic 200 escape preferentially removed <sup>36</sup>Ar relative to <sup>40</sup>Ar, then we have understated the loss of <sup>36</sup>Ar by impact erosion and 201 greater atmospheric pressures are required. However, nitrogen isotopes in ALH 84001 maskelynite are significantly 202 less fractionated than those in the modern Martian atmosphere<sup>17</sup>, which suggests that non-thermal escape occurring 203 throughout the past ~4 Ga, not early hydrodynamic escape, may be principally responsible for heavy isotope 204 enrichments. Therefore, because the modern Martian atmospheric <sup>38</sup>Ar/<sup>36</sup>Ar ratio is only enriched by 30% relative to 205 the primordial value<sup>1</sup>, 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<sup>26</sup> was used, then even 206 207 lower atmospheric pressures would be required (discussed above).

208 In summary, our model results indicate that atmospheric pressures during the Early to Middle Noachian were 209 likely less than ~1 bar. This suggests that a long-lived, CO<sub>2</sub>-based greenhouse atmosphere with surface 210 temperatures above the melting point of H<sub>2</sub>O did not exist at that time. The apparent absence of massive carbonate 211 deposits may be consistent with this result. The model results are also consistent with the observation that the 212 formation of phyllosilicates observed in the Noachian crust required low partial pressures of atmospheric  $CO_2^{11}$ . 213 Although it is possible that an extended greenhouse climate may have existed after the period of our meteoritic 214 constraint (i.e., after 4.16 Ga), geomorphic and spectral observations indicate that the Noachian was on average the 215 warmest and wettest period on Mars<sup>9,45</sup>. Therefore, if the trapped <sup>40</sup>Ar/<sup>36</sup>Ar ratio observed in ALH 84001 is a sample

216	of the Noachian Martian atmosphere, then even during this putative warm period it appears that water was only

217 intermittently stable in the liquid phase.

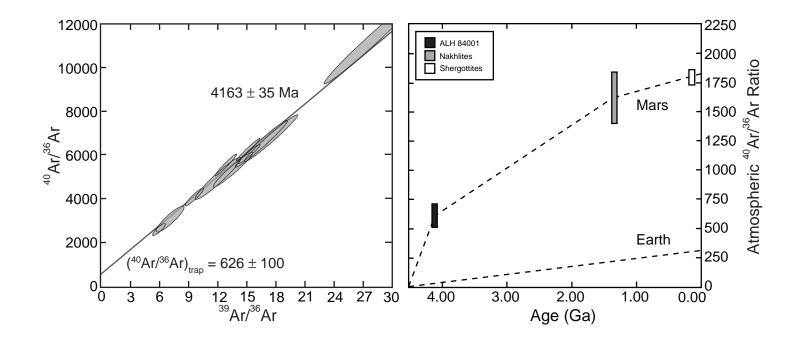
218	In	apact events or intense volcanism may have caused such intermittent conditions by delivering other
219	greenh	ouse gases to the atmosphere, such as SO <sub>2</sub> , $H_2S$ , and water vapor <sup>46</sup> . Given the partial pressures of CO <sub>2</sub>
220	permit	ted by our model results, temporarily elevated partial pressures of these other atmospheric gases (e.g., ~2 $\times$
221	10 <sup>-6</sup> ba	rs of $SO_2$ ) could have stabilized liquid water on Mars' surface at high latitudes <sup>15,16,47</sup> . The discovery of sulfate
222	deposi	ts in the Martian regolith underscores the potential role of $SO_2$ and $H_2S$ as greenhouse gases. Even in the
223	absenc	e of such gases, liquid water would be stable at low latitudes during seasonally warm periods given the partial
224	pressu	res of CO <sub>2</sub> permitted by our model results. Thus, existing observations of surface and meteorite mineralogy,
225	couple	d with the trapped Ar component identified in ALH 84001, suggest that the mean Noachian climate on Mars
226	was co	ol (below freezing) and dry (without liquid water), with only intermittent periods of warm and wet conditions.
227		
228		
229	Refere	nces
230	1	Jakosky, B. M. & Phillips, R. J. Mars' volatile and climate history. Nature 412, 237-244 (2001).
231	2	Pepin, R. O. Evolution of the Martian atmosphere. <i>Icarus</i> 111, 289-304 (1994).
232 233	3	Colaprete, A. & Toon, O. B. Carbon dioxide clouds in an early dense Martian atmosphere. <i>Journal of Geophysical Research</i> <b>108</b> , 6-1 (2003).
234 235	4	Pollack, J. B., Kasting, J. F., Richardson, S. M. & Poliakoff, K. The case for a wet, warm climate on early Mars. <i>Icarus</i> <b>71</b> , 203-224 (1987).
236 237	5	Yung, Y. L., Nair, H. & Gerstell, M. F. CO2 Greenhouse in the Early Martian Atmosphere: SO2 Inhibits Condensation. <i>Icarus</i> <b>130</b> , 222-224 (1997).
238 239	6	Segura, T. L., Toon, O. B., Colaprete, A. & Zahnle, K. Environmental effects of large impacts on Mars. <i>Science</i> <b>298</b> , 1977-1980 (2002).
240 241	7	Catling, D. C. & Leovy, C. Mars Atmosphere History and Surface Interactions. <i>Encyclopedia of the solar system</i> (2006).
242 243	8	Bandfield, J. L. Global mineral distributions on Mars. <i>Journal of Geophysical Research. E. Planets</i> <b>107</b> , 9-1 (2002).
244 245	9	Bibring, J. P. <i>et al.</i> Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data. <i>Science</i> <b>312</b> , 400 (2006).

246 247 248	10	Murchie, S. L. <i>et al.</i> A synthesis of Martian aqueous mineralogy after 1 Mars year of observations from the Mars Reconnaissance Orbiter. <i>Journal of Geophysical Research</i> <b>114</b> , 1-30, doi:10.1029/2009JE003342 (2009).
249 250	11	Chevrier, V., Poulet, F. & Bibring, J. P. Early geochemical environment of Mars as determined from thermodynamics of phyllosilicates. <i>Nature</i> <b>448</b> , 60-63 (2007).
251 252	12	Arvidson, R. E. <i>et al.</i> Spectral reflectance and morphologic correlations in eastern Terra Meridiani, Mars. <i>Science</i> <b>307</b> , 1591-1594 (2005).
253 254	13	Gendrin, A. <i>et al.</i> Sulfates in Martian layered terrains: the OMEGA/Mars Express view. <i>Science</i> <b>307</b> , 1587-1591 (2005).
255 256	14	Squyres, S. W. <i>et al.</i> In situ evidence for an ancient aqueous environment at Meridiani Planum, Mars. <i>Science</i> <b>306</b> , 1709-1714 (2004).
257 258	15	Halevy, I., Zuber, M. T. & Schrag, D. P. A sulfur dioxide climate feedback on early Mars. <i>Science</i> <b>318</b> , 1903 (2007).
259 260	16	Johnson, S. S., Mischna, M. A., Grove, T. L. & Zuber, M. T. Sulfur-induced greenhouse warming on early Mars. <i>Journal of Geophysical Research</i> <b>113</b> , E08005 (2008).
261 262	17	Bogard, D. D., Clayton, R. N., Marti, K., Owen, T. & Turner, G. Martian volatiles: isotopic composition, origin, and evolution. <i>Space Science Reviews</i> <b>96</b> , 425-458 (2001).
263 264 265	18	Cassata, W. S., Shuster, D. L., Renne, P. R. & Weiss, B. P. Evidence for shock heating and constraints on Martian surface temperatures revealed by 40Ar/39Ar thermochronometry of Martian meteorites. <i>Geochimica et Cosmochimica Acta</i> <b>74</b> , 6900-6920 (2010).
266 267	19	Begemann, F., Weber, H. W. & Hintenberger, H. On the primoridal abundance of argon-40. <i>Astrophys. J.</i> <b>203</b> (1976).
268 269	20	Lee, J. Y. <i>et al.</i> A redetermination of the isotopic abundances of atmospheric Ar. <i>Geochimica et Cosmochimica Acta</i> <b>70</b> , 4507-4512 (2006).
270 271	21	Brain, D. A. & Jakosky, B. M. Atmospheric loss since the onset of the Martian geologic record: Combined role of impact erosion and sputtering. <i>Journal of Geophysical Research</i> <b>103</b> , 22689-22694 (1998).
272 273	22	Melosh, H. J. & Vickery, A. M. Impact erosion of the primordial atmosphere of Mars. <i>Nature</i> <b>338</b> , 487-489 (1989).
274 275	23	Hutchins, K. S., Jakosky, B. M. & Luhmann, J. G. Impact of a paleomagnetic field on sputtering loss of Martian atmospheric argon and neon. <i>Journal of Geophysical Research</i> <b>102</b> , 9183-9189 (1997).
276 277	24	Roberts, J. H., Lillis, R. J. & Manga, M. Giant impacts on early Mars and the cessation of the Martian dynamo. <i>Journal of Geophysical Research</i> <b>114</b> , doi:10.1029/2008JE003287 (2009).
278 279	25	Weiss, B. P., Fong, L. E., Vali, H., Lima, E. A. & Baudenbacher, F. J. Paleointensity of the ancient Martian magnetic field. <i>Geophysical Research Letters</i> <b>35</b> , L23207 (2008).
280 281	26	Breuer, D. & Spohn, T. Viscosity of the Martian mantle and its initial temperature: Constraints from crust formation history and the evolution of the magnetic field. <i>Planetary and Space Science</i> <b>54</b> , 153-169 (2006).
282	27	Dreibus, G. et al. in Lunar and Planetry Science Conference XIII Vol. 13 186-187 (1982).

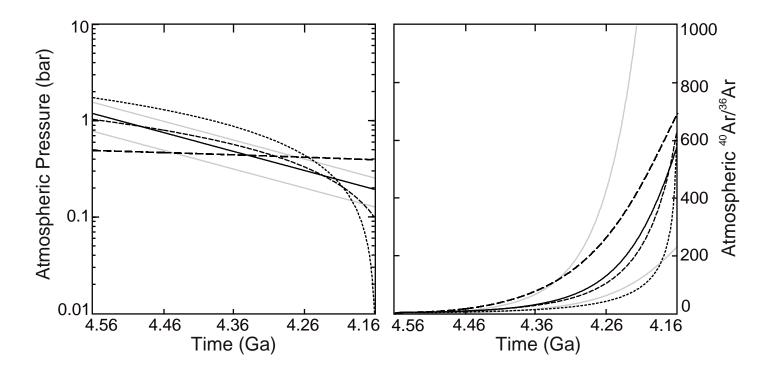
283 284	28	Taylor, G. J. <i>et al.</i> Bulk composition and early differentiation of Mars. <i>Journal of Geophysical Research</i> <b>111</b> , E03S10 (2006).
285 286	29	Boctor, N. Z., Wang, J., Alexander, C. M., Hauri, E. & Irving, A. J. in 68th Annual Meteoritical Society Meeting. 5261.
287 288	30	Hirschmann, M. M. & Withers, A. C. Ventilation of CO2 from a reduced mantle and consequences for the early Martian greenhouse. <i>Earth and Planetary Science Letters</i> <b>270</b> , 147-155 (2008).
289 290	31	Saal, A. E., Hauri, E. H., Langmuir, C. H. & Perfit, M. R. Vapour undersaturation in primitive mid-ocean- ridge basalt and the volatile content of Earth's upper mantle. <i>Nature</i> <b>419</b> , 451-455 (2002).
291 292	32	Boctor, N. Z., Wang, J., Alexander, C. M. & Hauri, E. in 37th Annual Lunar and Planetary Science Conference. 1412.
293 294	33	Neukum, G. & Wise, D. U. Mars-A standard crater curve and possible new time scale. <i>Science</i> <b>194</b> , 1381-1387 (1976).
295 296	34	Manning, C. V., McKay, C. P. & Zahnle, K. J. Thick and thin models of the evolution of carbon dioxide on Mars. <i>Icarus</i> <b>180</b> , 38-59 (2006).
297	35	McDonough, W. F. & Sun, S. S. The composition of the Earth. Chemical Geology 120, 223-253 (1995).
298 299	36	Zahringer, J. Primordial argon and the metamorphism of chondrites. <i>Earth and Planetary Science Letters</i> <b>1</b> , 379-382 (1966).
300 301	37	Owen, T. <i>et al.</i> The composition of the atmosphere at the surface of Mars. <i>Journal of Geophysical Research</i> <b>82</b> , 4635-4639 (1977).
302 303	38	Michalski, J. R. & Niles, P. B. Deep crustal carbonate rocks exposed by meteor impact on Mars. <i>Nature Geoscience</i> <b>3</b> , 751-755 (2010).
304 305	39	Morris, R. V. <i>et al.</i> Identification of carbonate-rich outcrops on Mars by the Spirit Rover. <i>Science</i> <b>329</b> , 421 (2010).
306 307	40	Christensen, P. R. <i>et al.</i> Initial results from the Mini-TES experiment in Gusev Crater from the Spirit rover. <i>Science</i> <b>305</b> , 837-842 (2004).
308 309	41	Boynton, W. V. <i>et al.</i> Evidence for calcium carbonate at the Mars Phoenix landing site. <i>Science</i> <b>325</b> , 61 (2009).
310	42	Owen, T. & Bar-Nun, A. Comets, impacts, and atmospheres. Icarus 116, 215-226 (1995).
311	43	Donahue, T. M. & Pollack, J. B. in Venus Vol. 1 1003-1036 (University of Arizona Press, 1983).
312	44	Anders, E. & Owen, T. Mars and Earth: Origin and abundance of volatiles. Science 198, 453-465 (1977).
313 314	45	Carr, M. H. & Head, J. W. Geologic history of Mars. <i>Earth and Planetary Science Letters</i> <b>294</b> , 185-203 (2010).
315 316	46	Toon, O. B., Segura, T. & Zahnle, K. The Formation of Martian River Valleys by Impacts. <i>Annual Review of Earth and Planetary Sciences</i> <b>38</b> , 303-322 (2010).
317 318	47	Tian, F. <i>et al.</i> Photochemical and climate consequences of sulfur outgassing on early Mars. <i>Earth and Planetary Science Letters</i> <b>295</b> , 412-418 (2010).

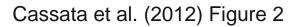
- 319 48 Sohl, F. & Spohn, T. The interior structure of Mars: Implications from SNC meteorites. Journal of 320 geophysical research 102, 1613-1635 (1997). 321 Lapen, T. et al. A younger age for ALH84001 and its geochemical link to shergottite sources in Mars. 49 322 Science 328, 347-351 (2010). 323 Bouvier, A., Blichert-Toft, J. & AlbarEde, F. Martian meteorite chronology and the evolution of the 50 324 interior of Mars. Earth and Planetary Science Letters 280, 285-295 (2009). 325 326 327 Acknowledgements 328 329 The authors acknowledge financial support from the NASA Mars Fundamental Research program (grant MFRP05-330 0108 to B.P.W. and D.L.S.), the NSF Petrology and Geochemistry program (grant EAR- 0838572 to P.R.R. and 331 D.L.S.), the NSF Major Research Instrumentation program (grant EAR-0618219 to D.L.S. and P.R.R), and the Ann 332 and Gordon Getty Foundation. W.S. Cassata was supported by a National Science Foundation Graduate Research 333 Fellowship, W.S. Cassata thanks Michael Manga, Edwin Kite, and Chris Huber for constructive discussions related 334 to this paper. 335 336 337 **Figure Captions** 338 339 **Figure 1:** (left) <sup>40</sup>Ar/<sup>39</sup>Ar isochron diagram for maskelvnite in ALH 84001-1 (redrafted from Cassata et al.<sup>18</sup>). 340 Correlation between the isotope ratios <sup>39</sup>Ar/<sup>36</sup>Ar and <sup>40</sup>Ar/<sup>36</sup>Ar measured during stepwise degassing of ALH 84001 341 constrains the non-radiogenic argon component "trapped" in the glass from the y-intercept and the age from the 342 slope. The isochron age (4.165  $\pm$  0.035 Ga) is indistinguishable at  $2\sigma$  from recently reported Lu-Hf (4.09  $\pm$  0.03  $Ga)^{49}$  and Pb-Pb (4.074 ± 0.099 Ga)<sup>50</sup> ages. The  ${}^{40}Ar/{}^{36}Ar$  ratio of the trapped component in ALH 84001 343
  - maskelynite is  $626 \pm 100$ . (**right**) Plot of the <sup>40</sup>Ar/<sup>36</sup>Ar ratios of trapped Ar components identified in Martian
  - 345 meteorites. ALH 84001 and Nakhlite data are from Cassata et al.<sup>18</sup>. Shergottite data are from Bogard et al.<sup>17</sup>. The
  - 346 Nakhlite <sup>40</sup>Ar/<sup>36</sup>Ar ratio represents the weighted average of MIL 03346 and Nakhla meteorites (see supplementary
  - 347 files). Earth's atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio is shown for comparison. Dashed lines linearly connect data points and
  - 348 do not represent the evolution of the atmospheric  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio on Earth or Mars.
  - 349

- 350 Figure 2: Modeled paleoatmospheric pressure paths (left) and corresponding evolution in the atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar 351 ratio (right) for the model parameters listed in Table 1. Dashed curves denote a constant rate of pressure change and 352 solid lines an exponential decrease. Four atmospheric pressure models that predict an  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratio within 626 ± 353 100 at 4.16 Ga are shown in black. For comparison, two models that fail to predict this ratio are shown in gray; an 354 array of additional scenarios excluded by the ALH 84001 data is shown in the supplementary files. Linearly 355 decreasing pressure paths were forced to evolve to pressures ranging between 10 mbar to 10 bar at 4.16 Ga; those 356 forced to final pressures >400 mbar predict  ${}^{40}$ Ar/ ${}^{36}$ Ar ratios less than  $626 \pm 100$  and are therefore excluded. For 357 clarity, only results for final pressures of 10 mbar, 100 mbar, and 400 mbar are shown. Exponential pressure models 358 decline at the same rate as the Martian impact flux<sup>22</sup> (see supplementary files), with  $\sim 16\%$  of the initial pressures at 359 4.16 Ga. The curves shown in black are representative of the range of permissible linear, exponential, and random 360 solutions (see Fig. S1) and require <1 bar of atmospheric pressure (on average) throughout most of the Early
- 361 Noachian. A detailed analysis of the model sensitivity to input parameters is given in the supplementary files.



Cassata et al. (2012) Figure 1





Parameter	Notation	Parameter Range <sup>a</sup>	Preferred Value	Unit	Ref.
Radius of Mars	r		3400 x 10 <sup>3</sup>	m	1
Mass of bulk sililcate Mars (BSM) <sup>b</sup>	m <sub>BSM</sub>		5.11 x 10 <sup>23</sup>	kg	2
Surface gravity	g		$1700 \ge 10^3$	$m/s^2$	1
K concentration in magmas	$[K]_{magma}$	1300-3300	2500	ppm	3,4
K concentration in impactors	[K] <sub>impact</sub>		550	ppm	5
<sup>36</sup> Ar concentration in impactors	[ <sup>36</sup> Ar] <sub>impact</sub>		15	ppt	6
$(N_2 + CO_2)$ concentration in magmas	[CN] <sub>magma</sub>	5-500	250	ppm	7,8,9
Magmatic ${}^{36}$ Ar/(N <sub>2</sub> + CO <sub>2</sub> ) ratio	$\mathbf{R}_{\mathrm{magma}}$	10-8-10-9	5 x 10 <sup>-9</sup>		10,11
Initial Atmospheric ${}^{36}Ar/(N_2 + CO_2)$ ratio	R <sub>atm</sub>	10-4-10-6	10-5		
Magma Flux <sup>°</sup>	$V_{magma}(t)$		B&S(2006)	kg/Ma	12
Magma density	$\rho_{magma}$		3000	kg/km <sup>3</sup>	
Impactor Flux <sup>d</sup>	$V_{impact}(t)$		M&V(1989)	kg/Ma	13,14

1: Sohl and Spohn (1997)<sup>48</sup>; 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 weight-% and BSM is 80 weight-%.

c: B&S(2006) is the crustal production model of Breuer and Spohn (2006) (see text for details).

d: M&V(1989) is the Martian impact flux derived by Melosh and Vickery (1989) (see text for details).

### **Supplementary Files for:**

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

William S. Cassata<sup>1,2,\*</sup>, David L. Shuster<sup>1,2</sup>, Paul R. Renne<sup>1,2</sup>, Benjamin P. Weiss<sup>3</sup>

- Department of Earth and Planetary Science, University of California Berkeley, 307 McCone Hall #4767, Berkeley, CA 94720-4767, USA (<u>cassata@berkeley.edu</u>)
- Berkeley Geochronology Center, 2455 Ridge Road, Berkeley, CA 94709, USA (<u>prenne@bgc.org</u>, <u>dshuster@bgc.org</u>)
- Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA (bpweiss@mit.edu)
- \* Corresponding author

# **Contents:**

# **Supplementary Discussions:**

**Discussion S1:** Calculation details

Discussion S2: The origin of trapped Ar in ALH 84001

# **Supplementary References**

# **Supplementary Figures**

Fig. S1: Illustration of the range of paleoatmospheric pressure paths explored.

Fig. S2: Illustration of the model sensitivity to the K concentration of extracted magmas.

Fig. S3: Illustration of the model sensitivity to the CO<sub>2</sub> and N<sub>2</sub> concentration of extracted magmas.

**Fig. S4:** Illustration of the model sensitivity to the <sup>36</sup>Ar concentration of extracted magmas.

Fig. S5: Illustration of the model sensitivity to the primordial concentration of atmospheric <sup>36</sup>Ar.

# **Supplementary Tables**

**Table S1:** <sup>40</sup>Ar/<sup>36</sup>Ar ratios of trapped components identified in ALH 84001, Nakhla, and MIL 03346.

### **Discussion S1: Calculation Details**

The generalized equation describing the atmospheric molar abundance of isotope X is given by

$$\frac{d^{X}Ar}{dt} = N_{X}\left(t\right) - \left({}^{X}Ar\frac{L(t)}{P(t)}\right).$$
 (Eq. S1)

In this section we define each term in Eq. (S1) and discuss our discretized implementation. A complete list of variables and the range of values explored can be found in Table 1.

**i.**)  ${}^{X}Ar$  is the atmospheric abundance of isotope X in moles or atoms.

At all  $t > t_0$ , <sup>*X*</sup>*Ar* reflects the integrated effects of production and loss. At  $t_0$ , the mass of atmospheric <sup>36</sup>Ar is given by

$$m_{36_0} = \frac{R_{atm} \cdot P_0 \cdot 4\pi r^2}{g}$$
 (Eq. S2)

where  $P_0$  is total atmospheric pressure at  $t_0$ , g is the gravitational constant (3.72 m/s<sup>2</sup>), r is the radius of Mars (3397 x 10<sup>3</sup> m), and  $R_{atm}$  is the atmospheric <sup>36</sup>Ar/(CO<sub>2</sub> + N<sub>2</sub>) ratio (i.e., the fractional abundance of atmospheric <sup>36</sup>Ar).  $P_0$  is a free parameter that is defined by hypothetical paleoatmospheric pressure paths. The molar abundance of atmospheric <sup>40</sup>Ar at  $t_0$  is simply 10<sup>-3</sup> times the molar abundance of atmospheric <sup>36</sup>Ar (Begemann et al., 1976).

**ii.**)  $N_X(t)$  is the rate of addition of isotope X to the atmosphere as a function of time due asteroid accretion and planetary degassing.

Asteroid Accretion:

To model the mass of <sup>40</sup>Ar added to the atmosphere by asteroids, we use 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), given by

$$m_{asteroid}\left(t\right) = 6.85 * 10^{12} \left(1 + 2300e^{-\left(\frac{10^3 * (4.56 - t)}{220}\right)}\right) \left(\frac{kg}{Ma}\right)$$
(Eq. S3)

where  $m_{asteroid}$  is the mass of asteroid material and *t* is time ranging from 4.56 to 4.16 Ga. The amount of asteroid-derived <sup>40</sup>Ar is given by

$${}^{40}Ar(t) = {}^{40}K_a \frac{\lambda_{\varepsilon}}{\lambda} \left( e^{-\lambda(4.56-t)} \right)$$
(Eq. S4)

where  ${}^{40}K_a$  is moles of  ${}^{40}$ K in a given mass of asteroid material,  $\lambda_{\varepsilon}$  is the partial decay constant for electron capture (0.576 x 10<sup>-1</sup> Ga<sup>-1</sup>) (Renne et al., 2011), and  $\lambda$  is the total decay constant (5.531 x 10<sup>-1</sup> Ga<sup>-1</sup>) (Renne et al., 2011). We assume that impacting asteroids contain a chondritic abundance of K (550 ppm; McDonough and Sun, 1995) and  ${}^{36}$ Ar concentrations typical of H-, L-, and LL-chondrites (~15 ppt; Zahringer, 1966).

#### Planetary degassing:

To model the production of atmospheric volatiles associated with surface, crustal, and upper mantle magmatic activity, we use the crustal production model of Breuer and Spohn (2006), approximated between 4.56 and 4.16 Ga by the following expression:

$$V_{magma}(t) = \left[ \left( 1.7075 * 10^3 \right) t^3 - \left( 2.1989 * 10^4 \right) t^2 + \left( 9.4408 * 10^4 \right) t - \left( 1.3512 * 10^5 \right) \right] \frac{km^3}{a}$$
(Eq. S5)

where *t* is time ranging from 4.56 to 4.16 Ga.

The mass of mantle-derived <sup>36</sup>Ar is given by

$$m_{36_{magma}}(t) = V_{magma}(t)\rho_{magma}[CN]_{magma}R_{magma}$$
(Eq. S6)

where  $\rho_{magma}$  is the magma density (3000 kg/m<sup>3</sup>), [*CN*]<sub>magma</sub> is the magmatic concentration of N<sub>2</sub> + CO<sub>2</sub>, and  $R_{magma}$  is the magmatic <sup>36</sup>Ar/(CO<sub>2</sub> + N<sub>2</sub>) ratio.

The molar production of <sup>40</sup>Ar is given by

$${}^{40}Ar(t) = {}^{40}K_m \frac{\lambda_{\varepsilon}}{\lambda} \left( e^{-\lambda(4.56-t)} \right)$$
(Eq. S7)

where  ${}^{40}K_m$  is moles of  ${}^{40}$ K in a given volume of magma. We modeled scenarios in which magmas contain between 1300 and 3300 ppm K (Table 1).

iii.)  $\frac{L(t)}{P(t)}$  is the fractional loss rate of atmospheric gases due to impact erosion, which we assume does not

fractionate isotopes or chemical species (Brain and Jakosky, 1998; Melosh and Vickery, 1989).

P(t) is atmospheric pressure (defined by the hypothetical paleoatmospheric pressure paths) and L(t) is the atmospheric pressure loss rate due to impact erosion, derived from the following equation:

$$\frac{dP}{dt} = I(t) - L(t), \tag{Eq. S8}$$

where I(t) is the rate of increase in atmospheric pressure resulting from planetary degassing, given by the following equation:

$$I(t) = \frac{V_{magma}(t)\rho_{magma}[CN]_{magma}g}{4\pi r^2}\frac{bar}{Ma}.$$
 (Eq. S9)

Thus L(t) can be extracted from the discretized version of equation Eq. (S8), given by

$$P(t) = P(t-dt) + dt(-L(t) + I(t)),$$
(Eq. S10)

where P(t) and P(t-dt) are two points on a hypothetical paleoatmospheric pressure path.

The discretized version of Eq. (S1) is then solved for both <sup>40</sup>Ar and <sup>36</sup>Ar according to the following:

$${}^{X}Ar(t) = \left(1 + dt \frac{L(t)}{P(t)}\right)^{-1} \left({}^{X}Ar(t - dt) + dtN_{X}(t)\right).$$
(Eq. S11)

#### **Discussion S2: The origin of trapped Ar in ALH 84001**

Critical to our argument is the assumption that the trapped argon component identified within maskelynite in ALH 84001 is atmospheric in origin and that it was acquired at 4.16 Ga. Although Xe isotopes in ALH 84001 confirm that atmospheric gas is present (Mathew et al., 1998; Swindle et al., 1995), it is conceivable that the <sup>40</sup>Ar/<sup>36</sup>Ar ratio of trapped gas within maskelynite (i) is contaminated by a mantle Ar component, (ii) is contaminated by a non-atmospheric upper crustal Ar component, or (iii) reflects a postcrystallization shock-implanted Ar component. We find these possibilities unlikely for reasons discussed below.

#### i.) A mantle Ar component

Argon is highly mobile in feldspars at temperatures as low as 300-400 °C (Cassata et al., 2009). As such, feldspars should continue to exchange Ar with the local environment during near-surface cooling, and are not expected to retain the isotopic composition of Ar in primary melts extracted from the Martian mantle, which have temperatures in excess of 1200 °C.

#### ii.) An upper crustal Ar component

Crystals generally incorporate excess argon as a result of (1) thermally-induced in-diffusion of grain boundary <sup>40</sup>Ar or (2) growth within magmas and interaction with fluids characterized by supraatmospheric  ${}^{40}$ Ar/ ${}^{36}$ Ar ratios. Given that three separate whole-rock fragments of ALH 84001 that each have different local maskelynite grain boundary environments and different grain size distributions yield indistinguishable trapped  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratios (Table S1), we consider it probable that maskelynite (or the precursor feldspar) equilibrated within a uniform Ar reservoir. When rocks are subjected to high a Ar pressure and an elevated <sup>40</sup>Ar/<sup>36</sup>Ar ratio produced by degassing of old, K-rich phases such as occurs in contact metamorphic aureoles (Harrison and McDougall, 1981; Renne et al., 1990) or in intrusions near such aureoles (Lanphere and Brent Dalrymple, 1976; Marzoli et al., 1999), the trapped "excess" <sup>40</sup>Ar component is generally manifest in step-heating experiments by anomalously high apparent ages derived from low temperature steps, which typically decrease with increasing extraction temperature. This implies a decreasing proportion of trapped relative to radiogenic Ar components, generally interpreted as being due to some combination of the trapped component being (i) surface-correlated, i.e. through inward diffusion, and (ii) sited in vacancies or microfractures with low activation energies (Harrison and McDougall, 1981). Thus post-crystallization in-diffusion of grain-boundary <sup>40</sup>Ar from degassing country rocks can be dismissed as a plausible source of Ar, as one would expect the trapped  $40^{40}$ Ar/36Ar ratio to be spatially variable.

If the trapped component observed in maskelynite reflects a uniformly distributed supra-atmospheric component, then the evolved parental magma to ALH 84001 must have incorporated and homogenized excess <sup>40</sup>Ar from upper crustal rocks, possibly through interactions with crustal groundwater and pore gases. Such a scenario seems unlikely, as the trapped <sup>40</sup>Ar/<sup>36</sup>Ar ratios observed in petrogenetically similar feldspathic phases in Shergottites and Nakhlites (Table S1) do not exceed the inferred atmospheric value of ~1800 (Bogard et al., 2001; Cassata et al., 2010). Moreover, in our experience, such cases of feldspar and glass contamination with argon having an appreciably (e.g., >20%) supra-atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio generally fail to produce well-defined isochrons because the trapped component is not isotopically

#### Supplementary Files

homogeneous. Trapped components of Ar in terrestrial plagioclase, in both extrusive and intrusive rocks, commonly have atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar compositions as indicated in flat apparent age spectra (Ernesto et al., 1999; Renne et al., 1996) wherein apparent ages are computed using an air correction.

iii.) A post-4.16 Ga shock-implanted Ar component

ALH 84001 appears to have been subjected to a significant shock event at ~1 Ga wherein both maskelynite and pyroxenes were locally heated to high temperatures, resulting in Ar loss (Cassata et al., 2010). Bogard et al. (1986) showed that unfractionated noble gases can be incorporated into crystals during such shock events. If the trapped <sup>40</sup>Ar/<sup>36</sup>Ar ratio observed within maskelynite reflects shock implanted atmospheric Ar associated with the  $\sim 1$  Ga event, then by implication the Martian atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio at ~1 Ga was ~600. However, the ~1.3 Ga Martian meteorites MIL 03346 and Nakhla yield a weighted average trapped  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratio of  $1600 \pm 200$ , which suggests the Martian atmospheric  $^{40}$ Ar/ $^{36}$ Ar ratio at ~1 Ga was much greater than 600 (Table S1; Cassata et al., 2010). If the trapped <sup>40</sup>Ar/<sup>36</sup>Ar reflects shock implanted Ar associated with a hitherto unrecognized shock event that occurred between 4.16 Ga and ~1 Ga, then it must have been implanted without disturbance to the distribution of radiogenic <sup>40</sup>Ar (see plateau in ALH-1 from Cassata et al., 2010), which requires shock pressures lower than 10-15 GPa (Bogard et al., 1988). At these low pressures, the implantation efficiency of atmospheric gases is greatly reduced (Bogard et al., 1986), and those gases that are implanted are degassed at low temperatures (i.e., they are surface correlated or contained within microfractures; Bogard et al., 1986). In ALH 84001, the trapped Ar component is pervasive, comprising more than 10% of the total <sup>40</sup>Ar in the highest temperature maskelynite extractions (see Cassata et al., 2010). As such, we find it unlikely that a minor shock event between 4.16 and ~1 Ga implanted the observed trapped component.

We hold that the simplest explanation for the trapping of Ar isotopes observed within maskelynite in ALH 84001 is equilibration with a near-atmospheric reservoir at 4.16 Ga.

# **Supplementary References**

Begemann, F., Weber, H.W., Hintenberger, H., 1976. On the primoridal abundance of argon-40. Astrophys. J. 203.

Bogard, D., Horz, F., Stoffler, D., 1988. Loss of radiogenic argon from shocked granitic clasts in suevite deposits from the Ries Crater. Geochimica et Cosmochimica Acta 52, 2639-2649.

Bogard, D.D., Clayton, R.N., Marti, K., Owen, T., Turner, G., 2001. Martian volatiles: isotopic composition, origin, and evolution. Space Science Reviews 96, 425-458.

Bogard, D.D., Horz, F., Johnson, P.H., 1986. Shock-implanted noble gases: An experimental study with implications for the origin of Martian gases in shergottite meteorites, 7th Lunar and Planetary Science Conference. Journal of Geophysical Research, pp. 99-114.

Brain, D.A., Jakosky, B.M., 1998. Atmospheric loss since the onset of the Martian geologic record: Combined role of impact erosion and sputtering. Journal of Geophysical Research 103, 22689-22694.

Breuer, D., Spohn, T., 2006. Viscosity of the Martian mantle and its initial temperature: Constraints from crust formation history and the evolution of the magnetic field. Planetary and Space Science 54, 153-169.

Cassata, W.S., Renne, P.R., Shuster, D.L., 2009. Argon diffusion in plagioclase and implications for thermochronometry: A case study from the Bushveld Complex, South Africa. Geochimica et Cosmochimica Acta 73, 6600-6612.

Cassata, W.S., Shuster, D.L., Renne, P.R., Weiss, B.P., 2010. Evidence for shock heating and constraints on Martian surface temperatures revealed by 40Ar/39Ar thermochronometry of Martian meteorites. Geochimica et Cosmochimica Acta 74, 6900-6920.

Ernesto, M., Raposo, M.I.B., Marques, L.S., Renne, P.R., Diogo, L.A., de Min, A., 1999. Paleomagnetism, geochemistry and Ar-40/Ar-39 dating of the North-eastern Parana Magmatic Province: tectonic implications. Journal of Geodynamics 28, 321-340.

Harrison, T.M., McDougall, I., 1981. Excess40Ar in metamorphic rocks from Broken Hill, New South Wales: implications for40Ar/39Ar age spectra and the thermal history of the region. Earth and Planetary Science Letters 55, 123-149.

Lanphere, M.A., Brent Dalrymple, G., 1976. Identification of excess 40Ar by the 40Ar/39Ar age spectrum technique. Earth and Planetary Science Letters 32, 141-148.

Manning, C.V., McKay, C.P., Zahnle, K.J., 2006. Thick and thin models of the evolution of carbon dioxide on Mars. Icarus 180, 38-59.

Marzoli, A., Renne, P.R., Piccirillo, E.M., Ernesto, M., Bellieni, G., De Min, A., 1999. Extensive 200million-year-old continental flood basalts of the Central Atlantic Magmatic Province. Science 284, 616-618.

Mathew, K., Kim, J., Marti, K., 1998. Martian atmospheric and indigenous components of xenon and nitrogen in the Shergotty, Nakhla, and Chassigny group meteorites. Meteoritics & Planetary Science 33, 655-664.

McDonough, W.F., Sun, S.S., 1995. The composition of the Earth. Chemical Geology 120, 223-253.

Melosh, H.J., Vickery, A.M., 1989. Impact erosion of the primordial atmosphere of Mars. Nature 338, 487-489.

Neukum, G., Wise, D.U., 1976. Mars-A standard crater curve and possible new time scale. Science 194, 1381-1387.

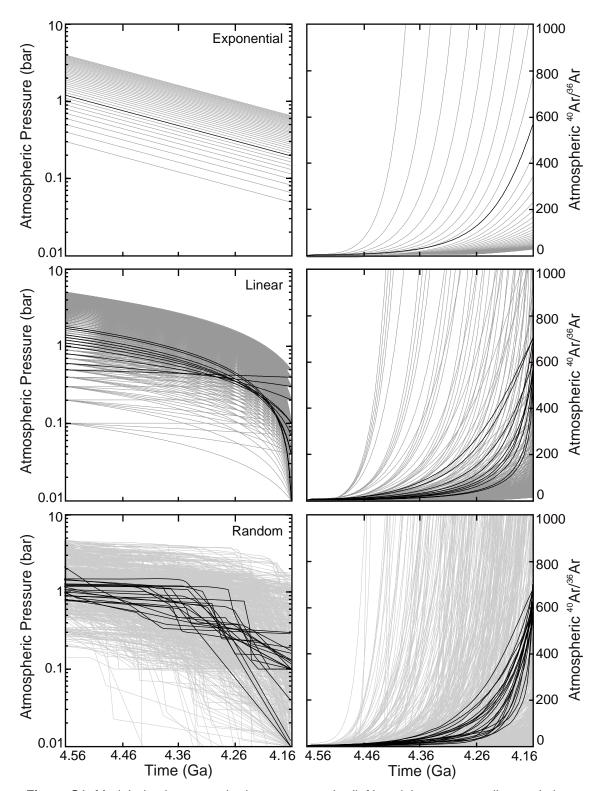
Renne, P.R., Balco, G., Ludwig, K., Mundil, R., Min, K., 2011. Response to the Comment by W. H. Schwarz et al. on "Joint determination of 40K decay constants and 40Ar\*/40K for the Fish Canyon sanidine standard, and improved accuracy for 40Ar/39Ar geochronology" by P.R. Renne et al. (2010). Geochimica et Cosmochimica Acta.

Renne, P.R., Deckart, K., Ernesto, M., Feraud, G., Piccirillo, E.M., 1996. Age of the Ponta Grossa dike swarm (Brazil), and implications to Parana flood volcanism. Earth and Planetary Science Letters 144, 199-211.

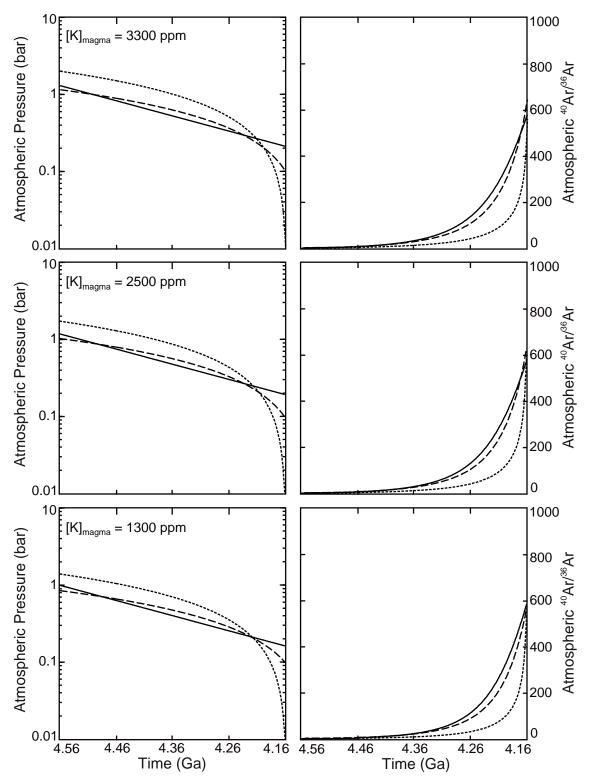
Renne, P.R., Onstott, T.C., D'Agrella-Filho, M.S., Pacca, I.G., Teixeira, W., 1990. 40Ar/39Ar dating of 1.0-1.1 Ga magnetizations from the Sa~ o Francisco and Kalahari cratons: tectonic implications for Pan-African and Brasiliano mobile belts. Earth and Planetary Science Letters 101, 349-366.

Swindle, T., Grier, J., Burkland, M., 1995. Noble gases in orthopyroxenite ALH84001: A different kind of martian meteorite with an atmospheric signature. Geochimica et Cosmochimica Acta 59, 793-801.

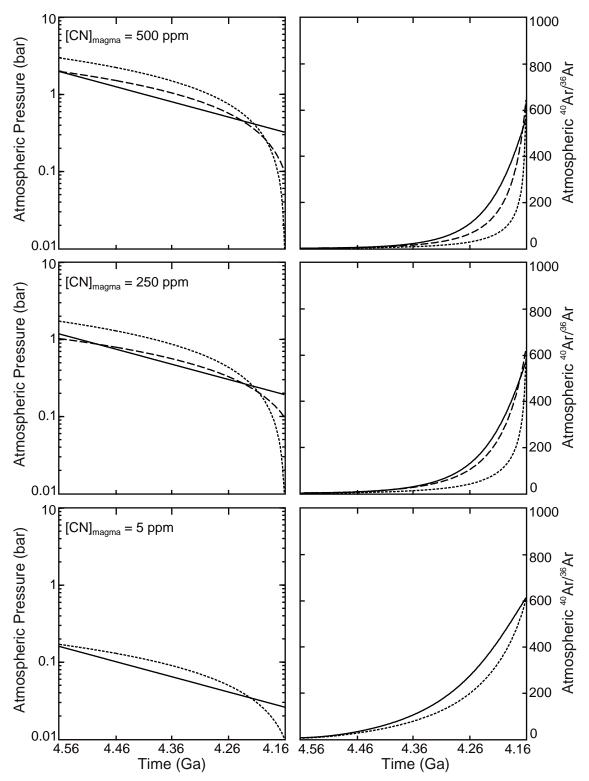
Zahringer, J., 1966. Primordial argon and the metamorphism of chondrites. Earth and Planetary Science Letters 1, 379-382.



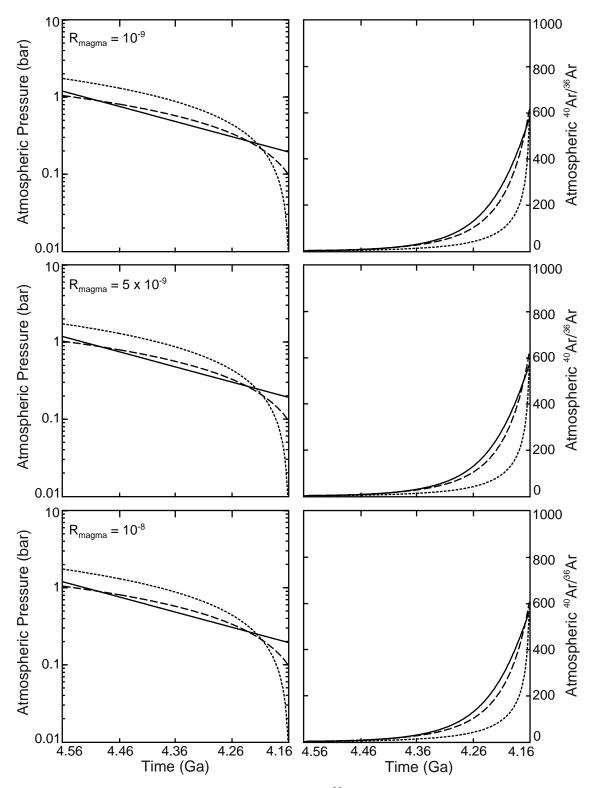
**Figure S1:** Modeled paleoatmospheric pressure paths (left) and the corresponding evolution in the atmospheric  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio (right) for the model parameters listed in Table 1. Atmospheric pressure models that predict an  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio within 626 ± 100 at 4.16 Ga are shown in black, and those that do not are shown in gray. Linearly decreasing models (middle) were forced to pressures of 10 mbar to 10 bar at 4.16 Ga; those forced to >400 mbar at 4.16 Ga predict  ${}^{40}$ Ar/ ${}^{36}$ Ar ratios lower than 626 ± 100 and are therefore excluded by the ALH 84001 data. Exponential pressure models (upper) decline at the same rate as the Martian impact flux (see text for details), with ~16% of the initial pressures at 4.16 Ga. Random pressure paths (lower) are well approximated by the linear and exponential models. The permissible solutions (shown in black) indicate that low atmospheric pressures (<1 bar on average) prevailed throughout the Early Noachian. In subsequent figures, only the results for exponential paths and linear paths with final pressure of 10 mbar and 100 mbar are shown.



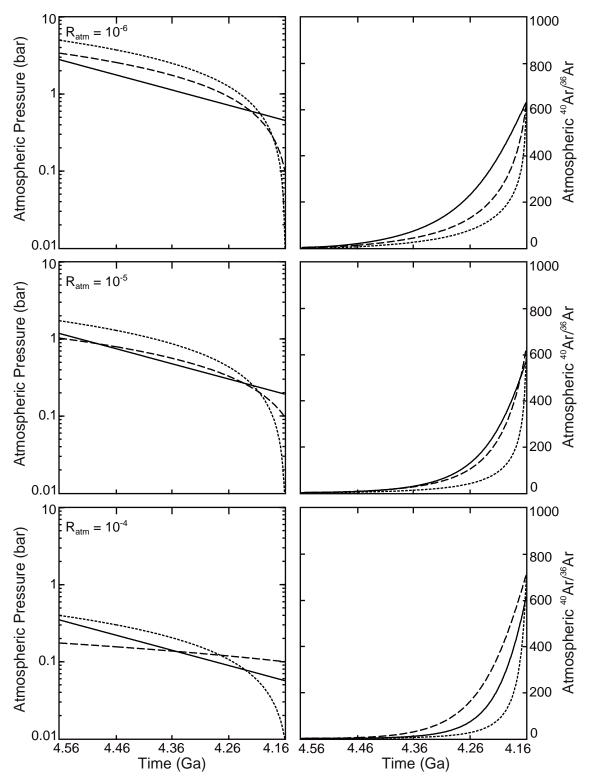
**Figure S2:** Illustration of the model sensitivity to the K concentration of extracted magmas. Magmas with higher concentrations of K, and therefore <sup>40</sup>Ar, more efficiently elevate the atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio. Thus higher atmospheric pressures (i.e., more atmospheric <sup>36</sup>Ar) are required to maintain a given <sup>40</sup>Ar/<sup>36</sup>Ar ratio if the magmatic K concentration is raised, and vice versa. The center panels represents our preferred model (modified from Fig. 2 in the main text), wherein the K concentration is 2500 ppm.



**Figure S3:** Illustration of the model sensitivity to the CO<sub>2</sub> and N<sub>2</sub> concentration of extracted magmas. Because magmatic  ${}^{36}$ Ar/(CO<sub>2</sub> + N<sub>2</sub>) ratios are lower than that of the primordial atmosphere (see text for discussion), magmas with higher concentrations of CO<sub>2</sub> and N<sub>2</sub> more efficiently dilute the concentration of atmospheric  ${}^{36}$ Ar. Thus higher atmospheric pressures (i.e., more primordial atmospheric  ${}^{36}$ Ar) are required to maintain a given  ${}^{40}$ Ar/ ${}^{36}$ Ar if the magmatic concentrations of CO<sub>2</sub> and N<sub>2</sub> are raised, and vice versa. The center panels represents our preferred model (modified from Fig. 2 in the main text), wherein [CN]<sub>magma</sub> is 250 ppm.



**Figure S4:** Illustration of the model sensitivity to the <sup>36</sup>Ar concentration of extracted magmas. Magmas with lower concentrations of <sup>36</sup>Ar more efficiently elevate the atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio. Thus higher atmospheric pressures (i.e., more atmospheric <sup>36</sup>Ar) are required to maintain a given <sup>40</sup>Ar/<sup>36</sup>Ar ratio if the magmatic concentration of <sup>36</sup>Ar is lowered, and vice versa. The center panels represents our preferred model (modified from Fig. 2 in the main text), wherein [CN]<sub>magma</sub> is 250 ppm.



**Figure S5:** Illustration of the model sensitivity to the primordial concentration of atmospheric <sup>36</sup>Ar. Magmas more efficiently elevate the atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio when the primordial concentration of atmospheric <sup>36</sup>Ar is lower. Thus higher atmospheric pressures are required to maintain a given <sup>40</sup>Ar/<sup>36</sup>Ar ratio if the primordial concentration of atmospheric <sup>36</sup>Ar is lowered, and vice versa. The center panels represents our preferred model (modified from Fig. 2 in the main text), wherein the primordial concentration of atmospheric <sup>36</sup>Ar is 10 ppb.

# Table S1: Summary of trapped <sup>40</sup>Ar/<sup>36</sup>Ar ratios

Sample	Phase	40Ar/3	${}^{86}Ar_i \pm 1\sigma$
ALH 84001 (4.16 ± 0	.04 Ga)		
ALH 84001-1	Maskelynite	626	± 100
ALH 84001-3	Maskelynite	694	± 230
ALH 84001-4	Maskelynite	514	± 450
ALH 84001-3	OPX	6	± 13
Nakhla (1.33 ± 0.02 (	Ga)		
Nakhla-1	Plagioclase	676	± 4900
Nakhla-2	Plagioclase	2119	± 670
Nakhla-5	Plagioclase	2430	± 570
Nakhla-1	CPX	42	± 10
Nakhla-2	CPX	58	± 30
Nakhla-4	CPX	-4	± 17
MIL 03346 (1.34 ± 0.0	01 Ga)		
MIL 03346-1	Mesostasis Glass	1425	± 230
MIL 03346-1	CPX	28	± 8

Data from Cassata et al. (2010)