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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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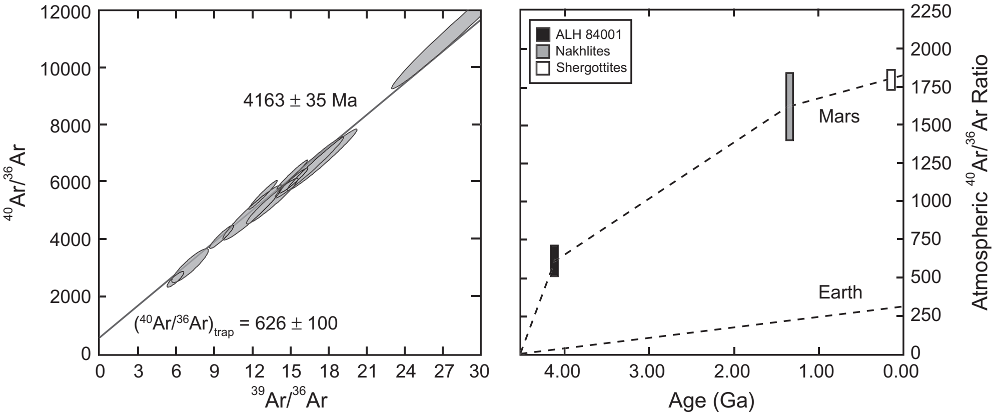

Fig. 1. Left: ^{40}Ar/^{39}Ar isochron diagram for maskelynite in ALH 84001-1 [redrafted from Cassata et al. (2010)]. Correlation between the isotope ratios ^{39}Ar/^{36}Ar and ^{40}Ar/^{36}Ar measured during stepwise degassing of ALH 84001 constrains the non-radiogenic argon component "trapped" in the 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:

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

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:

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

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-

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[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).