Meteorite constraints on Martian atmospheric loss and paleoclimate

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A B S T R A C T

The evolution of Mars' atmosphere to its currently thin state incapable of supporting liquid water remains poorly understood and has important implications for Martian climate history. Martian meteorites contain trapped atmospheric gases that can be used to constrain both the timing and effectiveness of atmospheric escape processes. In this paper, measurements of xenon isotopes in two ancient Martian meteorites, ALH 84001 and NWA 7034, are reported. The data indicate an early episode of atmospheric escape that mass fractionated xenon isotopes culminated within a few hundred million years of planetary formation, and little change to the atmospheric xenon isotopic composition has occurred since this time. In contrast, on Earth atmospheric xenon fractionation continued for at least two billion years (Pujol et al., 2011). Such differences in atmospheric Xe fractionation between the two planets suggest that climate conditions on Mars may have differed significantly from those on Archean Earth. For example, the hydrogen escape flux may not have exceeded the threshold required for xenon escape on Mars after 4.2–4.3 Ga, which indicates that Mars may have been significantly drier than Earth after this time.

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1. Introduction

At present, liquid water is not stable on Mars' surface due to low mean atmospheric pressures and temperatures. Whether Mars once possessed a long-lived, dense atmosphere and how its atmosphere evolved through time remain poorly understood. The vast depletion of volatiles in Mars' atmosphere relative to other terrestrial planets suggests that a significant portion of its volatile inventory was lost to space (Anders and Owen, 1977). The timescale over which volatiles were lost has important implications for Martian paleoclimate, and therefore whether the planet hosted warm and wet surface environments conducive to life.

Models of volatile loss have focused on three mechanisms: hydrodynamic escape (Hunten et al., 1987; Pepin, 1991; Zahnle and Kasting, 1986), impact erosion (Melosh and Vickery, 1989), and non-thermal escape (Jakosky et al., 1994; Pepin, 1994). Hydrodynamic escape is the acceleration of atmospheric hydrogen (H) beyond the planetary escape velocity as a result of extreme ultraviolet (EUV) radiation. Other atmospheric constituents are carried outward by collisions with escaping hydrogen, resulting in the preferential loss of light atoms and molecules (Hunten et al., 1987). An early, active epoch of the young Sun could have provided the intense EUV conditions required to drive hydrodynamic escape (Zahnle and Walker, 1982). Impact erosion is the acceleration of an impact-generated vapor plume beyond the planetary

escape velocity, resulting in the bulk (unfractionated) loss of atmospheric constituents in the plume (Melosh and Vickery, 1989). Loss of volatiles due to impact erosion is predicted to have been most significant early in solar system history, when the impactor flux was greatest (Melosh and Vickery, 1989). Non-thermal escape is the process by which neutral atoms and molecules in the upper atmosphere are converted to ions that exceed the planetary escape velocity (or that sputter neutral species to energies that exceed the escape velocity) by interactions with solar wind particles, EUV radiation, or electron impact (Jakosky et al., 1994; Spreiter and Stahara, 1980). Non-thermal escape processes have likely operated throughout Martian history and, like hydrodynamic escape, result in the preferential loss of light atoms and molecules (e.g., Jakosky et al., 1994). Trapped atmospheric gases in Martian meteorites and *in situ* observations of Mars' atmosphere provide constraints on the extent to which these processes have modified its atmosphere over time.

Xenon (Xe) isotopes in the present Martian atmosphere are mass fractionated relative to solar-like Xe in Mars' mantle, with significant heavy isotope enrichments (Conrad et al., 2016). This observation has been taken as evidence for early hydrodynamic escape on Mars, as light isotopes are preferentially lost to space during hydrodynamic escape and Xe is generally considered too heavy to be fractionated by other non-thermal escape processes that have operated throughout planetary history (Hunten et al., 1987; Jakosky and Jones, 1997; Swindle and Jones, 1997). When extrapolated to lighter masses, the magnitude of fractionation observed in atmospheric Xe isotopes indicates that other atmospheric species

(e.g., CO_2, N_2, Ar, etc.) would have been nearly completely lost (Hunten et al., 1987; Pepin, 1991). Estimates of the timescale over which this process may have occurred range from a few million to hundreds of millions of years (e.g., Jakosky and Jones, 1997; Zahnle, 1993). If such extensive hydrodynamic escape occurred, then putative warm and wet conditions that may have existed later in Martian history, during the Hesperian, require the growth of a secondary atmosphere.

Measurements of trapped Xe isotopes in the ∼4.2 Ga Martian meteorite ALH 84001 (Gilmour et al., 1998; Miura et al., 1995; Murty and Mohapatra, 1997; Swindle et al., 1995), which likely reflect Mars' atmosphere at 4.0 Ga or earlier, were initially thought to provide empirical support for hydrodynamic escape on Mars (Murty and Mohapatra, 1997). Murty and Mohapatra (1997) suggested that trapped atmospheric Xe in ALH 84001 is indistinguishable from modern atmospheric Xe, and is therefore consistent with hydrodynamic fractionation occurring prior to the formation of ALH 84001. It has since been shown that trapped Xe in ALH 84001 is distinct from modern atmospheric Xe (Gilmour et al., 1998; Mathew and Marti, 2001). In the most detailed study published to date, Mathew and Marti (2001) suggested that Xe in ALH 84001 represents a mixture of ^{244}Pu-derived spontaneous fission Xe with a solar-like (unfractionated) Xe component. Their conclusion presents challenges for the early hydrodynamic escape hypothesis, as the bulk of atmospheric loss to space is implicated to post-date the age of ALH 84001 (Jakosky and Phillips, 2001).

Extreme ultraviolet (EUV) conditions were likely sufficient to drive hydrodynamic escape early in Martian history (Lammer et al., 2013; Ribas et al., 2005). Apparently unfractionated Xe isotopes in ALH 84001 (Mathew and Marti, 2001) therefore require a relatively hydrogen-deficient early Martian atmosphere, or an early stage of hydrodynamic escape that removed essentially all atmospheric Xe (and by implication other atmospheric constituents), followed by the formation of a secondary atmosphere comprising outgassed mantle volatiles. Additionally, a mechanism to fractionate Xe isotopes in lower EUV environments that prevailed after the formation of ALH 84001 is required. Evidence for the existence of such a process can be found on Earth, where atmospheric Xe isotopes in Archean rocks indicate that fractionation was a gradual process that occurred over at least two billion years (Pujol et al., 2011; Srinivasan, 1976). Catling and Zahnle (2009) and Zahnle (2015) proposed that in low EUV environments that prevailed after the Hadean, Xe may have been fractioned via ionic coupling with escaping H, which requires significantly lower H escape fluxes than required for neutral Xe escape.

Clearly important questions regarding the mechanisms by which and timescales over which Mars' atmosphere evolved remain unresolved. Constraints on the loss of Mars' primary atmosphere and potential growth of a secondary atmosphere resulting from magmatic outgassing have important implications for the climate history of Mars. In this paper, measurements of Xe isotopes in two ancient Martian meteorites, ALH 84001 and NWA 7034, are reported. These data, along with a revised interpretation of published data obtained from ALH 84001, provide new insights into the evolution of the ancient Martian atmosphere. The measurements suggest that an early episode of atmospheric escape extensively fractionated Xe isotopes within a few hundred million years of planetary formation, and little change has occurred since this time. The resulting implications for atmospheric evolution and climate on Mars during the Noachian and Hesperian are discussed.

2. Methods

Previous measurements of noble gases in ALH 84001 indicate that significant differences in the relative proportions of different trapped components are observed in analyses of relatively large samples [100's of mg; summarized in Mathew and Marti, 2001]. The elemental and isotopic compositions of individual aliquots contain varying contributions of end-member components defined by Martian interior and atmospheric gases (Mathew and Marti, 2001). Such significant differences in the relative proportions of trapped components in this relatively fine-grained sample suggest that at least one component is spatially localized (i.e., variably abundant in individual 100–1000 mg aliquots). The implication is that by reducing the mass of analyzed samples it is possible to minimize the relative abundance of one or more spatially localized components, and therefore more clearly define the isotopic composition of the other end-member(s). For this reason, <25 mg-sized aliquots of the two most ancient Martian meteorites, orthopyroxenite ALH 84001 (1 aliquot) and polymict breccia NWA 7034 (3 aliquots), were targeted for analysis. Because of the smaller sample sizes, individual extractions yield less precise isotopic measurements than previously reported analyses on larger aliquots.

Xe, Kr, and Ar isotopic measurements were performed in the Livermore Noble Gas Lab at Lawrence Livermore National Laboratory. Whole-rock fragments of ALH 84001 and NWA 7034, devoid of any saw cuts and fusion crust and weighing 8–22 mg, were loaded into small metal packets made from high-purity Pt–Ir tubes, crimped at both ends to create an encapsulating envelope, and placed into an ultra-high vacuum system beneath a sapphire view port. Samples were heated with a 75 W diode laser ($\lambda = 810 \pm 10$ nm) focused onto the metal envelope and coaxially aligned with an optical pyrometer. The single-color pyrometer was calibrated against a type-K thermocouple between ∼500 and 1200 °C following procedures described in Cassata and Borg (2016). During experimental heating, the samples were held at temperatures between ∼500 and 1600 °C for durations of 180 seconds. Additional details regarding this diode laser heating procedure are given in Cassata and Borg (2016). The released gas was purified using four SAES getters (two hot and two cold), analyzed using a Nu Instruments *Noblesse* mass spectrometer equipped with six Faraday cup detectors and four ion-counting, discrete dynode multiplier detectors. Samples were analyzed statically in peak hopping mode using the axial multiplier detector and were corrected for spectrometer discrimination and extraction line blanks. Sample analyses were bracketed by analyses of a Xe–Kr–Ar spike of known abundance and isotopic composition (atmospheric Ar and mass fractionated atmospheric Xe and Kr) to monitor for time dependent changes in spectrometer sensitivity and mass discrimination.

Cosmogenic corrections were applied to all Xe, Kr, and Ar isotopic measurements. The relative contributions of trapped and cosmogenic Xe were determined from a two-component deconvolution of the measured $^{124}Xe/^{130}Xe$ ratio assuming cosmogenic $^{124}Xe/^{130}Xe = 0.62$ (Marti et al., 1966) and trapped $^{124}Xe/^{130}Xe = 0.0258$ (Conrad et al., 2016).[1] A proportional abundance of cosmogenic Xe was then subtracted from other isotopes based on the isotopic composition of spallation Xe in Stannern, given by 124:126:128:129:130:131:132:134:136 = 0.60:1:1.45:1.50:0.97:2.80:0.90:0.25:0 (Marti et al., 1966). To determine the abundance of trapped Kr, all ^{86}Kr was assumed to be atmospheric (i.e., not cosmogenic) and proportional abundances of $^{78-84}Kr$ were assigned to this component based on the isotopic composition of Martian Kr (Pepin, 1991). The residual abundances of $^{78-84}Kr$ were assumed to be cosmogenic. The relative contributions of trapped and cosmogenic Ar were determined from a two-component deconvolution of the measured $^{38}Ar/^{36}Ar$ ratio assuming cosmogenic $^{38}Ar/^{36}Ar = 1.54$

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[1] The assumed isotopic composition of atmospheric Xe has a negligible effect on the inferred abundances of trapped ^{129}Xe, ^{132}Xe, ^{134}Xe, and ^{136}Xe, as the cosmogenic component is <5% of the total signal of these isotopes. Additionally, the observation that the heavy isotopes of Xe are indistinguishable from modern Martian atmosphere (discussed below) justifies this assumption.