Icarus 272 (2016) 212–227

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

Argon isotopes as tracers for martian atmospheric loss

Marek Slipski[a,b,*], Bruce M. Jakosky[b,c]

[a] Department of Astrophysical and Planetary Sciences, University of Colorado Boulder, Boulder, CO 80303, USA
[b] Laboratory for Atmospheric and Space Physics, 3665 Discovery Dr., Boulder, CO 80303, USA
[c] Department of Geological Science, University of Colorado Boulder, Boulder, CO 80303, USA

ARTICLE INFO

Article history:
Received 17 August 2015
Revised 5 February 2016
Accepted 25 February 2016
Available online 4 March 2016

Keywords:
Mars, atmosphere
Atmospheres, evolution
Abundances, atmospheres

ABSTRACT

Recent measurements of the present-day Ar abundance and isotopic ratios in the martian atmosphere by the SAM instrument suite onboard the Curiosity rover can be used to constrain the atmospheric and volatile evolution. We have examined the role of volcanic outgassing, escape to space via sputtering, crustal erosion, impact delivery, and impact erosion in reproducing the Ar isotope ratios from an initial state 4.4 billion years ago. To investigate the effects of each of these processes, their timing, and their intensity we have modeled exchanges of Ar isotopes between various reservoirs (mantle, crust, atmosphere, etc.) throughout Mars' history. Furthermore, we use present-day atmospheric measurements to determine the parameter space consistent with observations. We find that significant loss to space (at least 48% of atmospheric ^{36}Ar) is required to match the observed ^{36}Ar/^{38}Ar ratio. Our estimates of volcanic outgassing do not supply sufficient ^{40}Ar to the atmosphere to match observations, so in our model at least 31% of ^{40}Ar produced in the crust must have also been released to the atmosphere. Of the total ^{40}Ar introduced into the atmosphere about 25% must have been lost to space. By adding the present-day isotopic abundances with our results of total integrated Ar loss we find a "restored" value of atmospheric ^{40}Ar/^{36}Ar, which represents what that ratio would be if the total integrated Ar loss had remained in the atmosphere. We determine the restored value to be ~900–1500. This is below the present martian atmospheric value (1900 ± 300), but 3–5 times greater than the terrestrial value.

1. Introduction

Evidence for liquid water on Mars prior to 3.8 billion years ago (Gya) continues to build, motivating studies of its early atmospheric history and the conditions that could have existed to enable water to flow on the surface. The current low atmospheric pressure and temperature cannot support liquid water, though several mechanisms have been proposed that could have generated temperatures above freezing in the past (Johnson, Mischna and Grove, 2008; Pollack, Kasting and Richardson, 1987; Ramirez, Kopparapu and Zugger, 2014; Segura, Toon and Colaprete, 2002). Though debate continues over whether the observed fluvial features were formed during several hundred million years of warm conditions or shorter transient warm periods generated by large impacts, there is no doubt that the atmosphere has changed drastically from its initial state 4.5 Gya as a result of several important processes such as volcanic outgassing, interaction with the surface, and escape to space. Isotopic ratios of various atmospheric volatiles are fractionated through these processes, leaving an imprint of the atmosphere's evolution. Measurements of atmospheric H, C, O, N, and Ar show an enrichment in heavy isotopes relative to Earth isotopic ratios (Atreya, Trainer and Franz, 2013; Bogard, Clayton and Marti, 2001; Krasnopolsky, Mumma and Randall Gladstone, 1998; Owen, Biemann and Biller, 1977; Webster, Mahaffy and Flesch, 2013). This is striking evidence that loss of Mars' atmosphere to space has occurred (Jakosky, 1991; Jakosky, Pepin and Johnson, 1994). Lighter isotopes diffusively separate and are preferentially removed either by thermal processes (Jeans escape) in the case of H, or non-thermal processes such as dissociative recombination and collisions via impingement of the solar wind (Chassefière and Leblanc, 2004).

Indeed, measurements of the ratios of ^{36}Ar, ^{38}Ar, and ^{40}Ar in the present-day atmosphere (by Viking and the Mars Science Laboratory, MSL) and of the past atmosphere (through meteorites) are robust indications of significant Ar loss (Jakosky, Pepin and Johnson, 1994). These observations are displayed in Table 1. The value of ^{36}Ar/^{38}Ar in Earth's atmosphere is nearly equivalent to the ratio in the solar wind, asteroids, and Jupiter's atmosphere; that is, Earth's ^{36}Ar/^{38}Ar is primordial. Assuming the source of

* Corresponding author at: Laboratory for Atmospheric and Space Physics, 3665 Discovery Dr., Boulder, CO 80303, USA.
E-mail address: marek.slipski@colorado.edu (M. Slipski).

http://dx.doi.org/10.1016/j.icarus.2016.02.047
0019-1035/

Table 1
Measurements of the atmospheric Ar isotope ratios and abundances from various sources. The meteorite measurements come from the trapped gas impact melts. Earth's atmospheric values are shown for reference.

	Ar mixing ratio	^{36}Ar/^{38}Ar	^{40}Ar/^{36}Ar	Age
MSL	0.0193 ± 0.0003[a]	4.2 ± 0.1[b]	1900 ± 300[a]	Present-day
Viking[c]	0.016	5.5 ± 1.5	3000 ± 500	Present-day
Shergottites[d]		4.1 ± 0.1	1800 ± 100	< 0.2 Gya
Nakhlites[d]			1615 ± 203	1.33 ± 0.02 Gya
ALH 84001[e]			626 ± 100	4.16 ± 0.04 Gya
Solar wind[f]		5.501 ± 0.014		Present-day
CI Chondrites[g]		5.30 ± 0.05		Primitive
Jupiter[h]		5.6 ± 0.25		Present-day
Earth[i]	0.0093	5.305 ± 0.002	298.56 ± 0.31	Present-day

[a] Mahaffy, Webster and Atreya (2013).
[b] Atreya, Trainer and Franz (2013).
[c] Owen, Biemann and Biller (1977).
[d] Bogard, Clayton and Marti (2001).
[e] Cassata, Shuster and Renne (2010).
[f] Pepin, Schlutter and Becker (2012), see also Vogel, Heber and Baur (2011).
[g] Pepin (1991).
[h] Mahaffy, Niemann and Alpert (2000).
[i] Lee, Marti and Severinghaus (2006).

atmospheric argon on both planets was the same (be it volcanic outgassing or asteroids and comets) the lower ratio of ^{36}Ar/^{38}Ar in the martian atmosphere can only be explained by loss to space. The ratio of ^{40}Ar/^{36}Ar in the martian atmosphere today also shows an enrichment in the heavy isotope (^{40}Ar/^{36}Ar $\sim$6 times the value in Earth's atmosphere), though interpreting this ratio is slightly more complicated as ^{40}Ar is produced by the decay of ^{40}K in the mantle and crust and is supplied to the atmosphere over time.

Motivated by recent confirmation of the enrichment of heavy isotopes in Mars' atmosphere and ongoing measurements of the upper atmosphere by the Mars Atmospheric and Volatile EvolutioN (MAVEN) mission, we sought to investigate atmospheric loss by modeling the evolution of Ar isotopic ratios through time. To do this, exchanges of volatiles between the atmosphere and other reservoirs—the mantle, the crust, and impactors—must be considered in addition to escape processes because they have certainly affected the atmospheric ratios as well, whether they have operated throughout Mars' history or only for a brief period. The complexity of the problem is somewhat alleviated for Ar compared to H, C, O, and N because as a noble gas, the available exchange pathways are limited; a model of the other gases would also need to include interactions of the atmosphere with the polar caps and the regolith. Since the time-variability of all the processes mentioned are poorly constrained, each one further amplifies the uncertainty in the model. Thus, by studying Ar we can build an understanding of a few important drivers of atmospheric evolution, how they have affected isotopic ratios through time, and what the present-day ratios imply about total atmospheric loss.

We constructed a box model in which Ar is exchanged between various reservoirs through time considering several processes. ^{40}Ar is produced by radioactive decay of ^{40}K in the mantle and the crust and is volcanically outgassed along with ^{36}Ar and ^{38}Ar. Once in the atmosphere, all the isotopes are subject to removal through interaction with the solar wind. In addition, impactors during the late heavy bombardment (LHB) and thereafter act as both a source and a (non-fractionating) sink. We assume a range of time-variable intensities for each of these processes and march from 4.4 Gya to the present.

The remainder of this paper is structured as follows: We first describe the model in Section 2, explain how it improves upon past models, detail the initial conditions of the various reservoirs, and justify the use of the time-dependent rates assumed for each exchange process. Then in Section 3 we explain outputs of the model by (a) building an intuition for the various processes by showing how each affects Ar isotope ratios in the absence of any other processes, (b) showing the interplay between various processes as they are combined in the model together, and (c) using present-day atmospheric measurements as model constraints to determine the parameter space consistent with observations. Finally, in Section 4 we discuss a few noteworthy consequences of the model.

2. Model

In this section, we explain the details of our box model (illustrated in Fig. 1) which consists of three main reservoirs in the system through which Ar is exchanged: the mantle, crust, and atmosphere. We describe the mantle reservoir and the processes that affect its Ar inventory—radioactive decay of ^{40}K, volcanic outgassing, and growth rate of the crust. Similarly, we discuss the initial conditions of the crustal reservoir and how ^{40}Ar is released into the atmosphere. This is followed with a justification of the range of escape rates of atmospheric Ar used and an explanation of how we include impact delivery and impact erosion in the model. All initial conditions and rates described in this section are listed in Table 2 for reference. The abundance of Ar in each reservoir, r, evolves according to:

$$\frac{d\,{}^{X}\mathrm{Ar}_r}{dt} = \sum_n [S_n(t) - L_n(t)] \tag{1}$$

For each isotopic species of argon—^{X}Ar where X can be 36, 38, or 40—the change in abundance with time of that species in a particular reservoir is equal to the supply rate of argon to that reservoir, S, minus the loss rate from the reservoir, L for each process, n, at time t. This allows for investigation of the evolution of ^{36}Ar, ^{38}Ar, and ^{40}Ar abundances and isotopic ratios in each reservoir. The model progresses forward in time for 4.4 Gyr (gigayears) in steps of 1 Myr. The argon isotopic abundances are calculated at each timestep and the content of each reservoir is updated. Similar approaches have been taken by Pepin (1994), Hutchins and Jakosky (1996) (two-reservoir system), Cassata, Shuster and Renne (2012) (early ^{40}Ar/^{36}Ar), Leblanc, Chassefière and Gillmann (2012) (^{40}Ar only), and Pujol, Marty and Burgess (2013) (Earth). However, none have considered all three isotopes simultaneously, used broad ranges of escape, outgassing, and CO_2 histories, or included the effects of impact delivery and erosion.