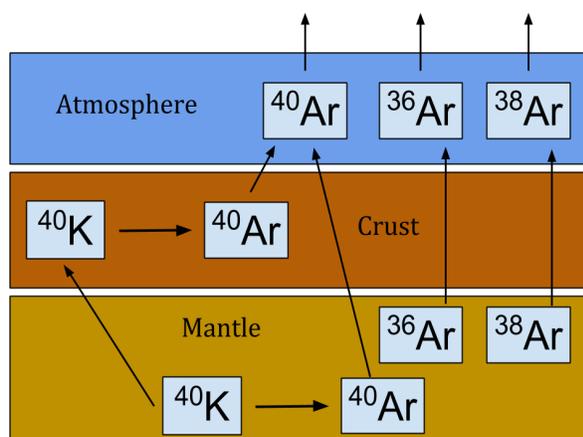


**EVOLUTION OF ARGON ISOTOPES IN THE MARTIAN ATMOSPHERE.** M. Slipski<sup>1,2</sup> and B. M. Jakosky<sup>2,3</sup>, <sup>1</sup>Department of Astrophysical and Planetary Sciences, University of Colorado Boulder (marek.slipski@colorado.edu), <sup>2</sup>Laboratory for Atmospheric and Space Physics, <sup>3</sup>Department of Geological Sciences, University of Colorado Boulder (bruce.jakosky@lasp.colorado.edu)

**Introduction:** Evidence for past water on Mars suggests that its climate was remarkably different four billion years ago. Isotope ratios of various volatiles in the Martian atmosphere are important for understanding the evolution of the atmosphere. Processes that cause an exchange of volatiles between the atmosphere and non-atmospheric reservoirs - such as volcanic outgassing from the interior, escape to space, impact delivery, and mixing with the crust - can fractionate isotopes. Thus, measurements of the present-day atmosphere reflect the importance of these exchanges over billions of years. Recent measurements of the present-day argon abundance and isotope ratios in the Martian atmosphere by the SAM instrument suite onboard the Curiosity rover [1,2] can be used to constrain the atmospheric and volatile evolution.

Argon is an important atmospheric tracer because once in the atmosphere the only loss process is escape to space, limiting the exchange pathways that become complicated for most volatiles. Here, we use a box model to study the evolution of Martian atmospheric argon. This model allows us to examine the effects of sputtering, outgassing, impact erosion and delivery, and crustal erosion on <sup>36</sup>Ar, <sup>38</sup>Ar, and <sup>40</sup>Ar abundances.

**Model:** The box model presented here examines the role of outgassing, escape to space via sputtering, impacts, and crustal erosion in reproducing the argon isotope ratios from an initial state 4.4 Gyr ago (Fig 1).



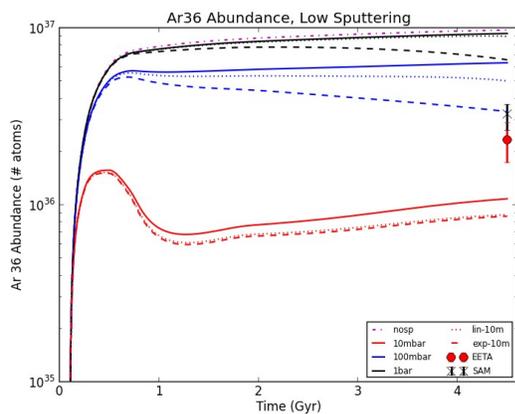
**Figure 1: A schematic diagram of the reservoirs and processes affecting abundances of argon isotopes.**

<sup>36</sup>Ar, <sup>38</sup>Ar, and <sup>40</sup>Ar are degassed from the mantle over time with initial planetary abundances of <sup>36</sup>Ar and <sup>38</sup>Ar in the mantle proportional to the concentration currently in Earth's atmosphere (though this initial concentration can be adjusted by a multiplicative factor). The radioactive decay of <sup>40</sup>K in the mantle and crust produces <sup>40</sup>Ar. The crustal production rate determines the amount of <sup>40</sup>K that is transported from the mantle and the amount of argon degassed into the atmosphere. An enrichment of <sup>40</sup>K in the crust enables additional <sup>40</sup>Ar to be released to the atmosphere from erosion.

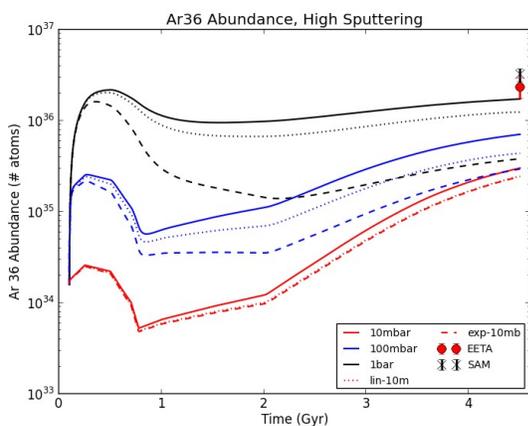
Once in the atmosphere, all argon species are subject to sputtering by collisions of solar-wind-produced O<sup>+</sup> pickup ions at the exobase. Lighter atoms have a larger scale height and, thus, are more abundant at the exobase causing higher fractionation. We calculate the escape rate for argon isotopes over billions of years by scaling from estimates of the amount of CO<sub>2</sub> sputtered [3]. This loss to space depends strongly on the amount of CO<sub>2</sub> in the atmosphere, the CO<sub>2</sub> sputtering rate evolution [4,5], and the time of the disappearance of the magnetic field.

Impacts during the Late Heavy Bombardment erode the atmosphere, but also deliver volatiles. Impact erosion is a non-fractionating process, but can remove a substantial portion of the atmosphere. However, the amount of volatiles delivered into the atmosphere from the same impacts may play a more important role. This delivery has two effects: the impactor argon isotopic ratio reduces the atmospheric <sup>36</sup>Ar/<sup>38</sup>Ar and the increase in other species at the exobase slows the rate at which argon is sputtered by pickup ions.

**Discussion:** Though the efficiency of argon sputtering is dependent on the evolution of CO<sub>2</sub>, we do not consider a parallel treatment of atmospheric CO<sub>2</sub>. Its evolution is complicated as several additional processes must be considered, which we have yet to model. Thus, we choose several atmospheric CO<sub>2</sub> histories, which are either plausible or useful end-members. Independently, we use end-member CO<sub>2</sub> sputtering rate histories. Figures 2 and 3 show how the evolution of atmospheric argon varies for different sputtering efficiencies and CO<sub>2</sub> amounts. With the prescribed outgassing model, we find 67% of <sup>36</sup>Ar transferred from the mantle to the atmosphere must have been lost to space to match the present-day abundance.



**Figures 2 and 3: Evolution of the  $^{36}\text{Ar}$  abundance for low (above) and high (below) sputtering rates with different initial  $\text{CO}_2$  abundances (in mbar) – 10 (red), 100 (blue), and 1000 (black) – and three  $\text{CO}_2$  histories – constant (solid), linearly decreasing (dotted), and exponentially decreasing (dashed).**



We also investigate the effect of an ancient magnetic field. We assume such a field could have lasted until 4.0 Gyr ago and disappeared in less than 1 Myr, preventing argon from leaving the atmosphere during this time. In the model, Ar sputtering and  $\text{CO}_2$  losses are delayed until the magnetic field has been removed. We find this changes the evolution of atmospheric argon insignificantly over the last 4.0 Gyr. As a result of efficient sputtering early in Mars' history, in under 1 Gyr argon abundances return to values near those found for no delay in sputtering. However, a delay lowers the upper limit of initial  $\text{CO}_2$  pressure able to reproduce present-day argon abundances

Our outgassing model cannot reproduce the present-day abundance of  $^{40}\text{Ar}$  even when sputtering is ignored. Thus, an additional source must be considered. In the model, the crust is enriched in  $^{40}\text{K}$ , so erosion of the crust supplies  $^{40}\text{Ar}$  to the atmosphere

without changing  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  abundances. We vary the efficiency of this erosion to determine how much  $^{40}\text{Ar}$  must be transferred into the atmosphere. For calculations that reproduce the  $^{36}\text{Ar}$  abundance and the  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio, we find that 27-36% of  $^{40}\text{Ar}$  produced in the crust must have been released to the atmosphere by erosion and about 33% of the  $^{40}\text{Ar}$  released from the mantle and crust must have been lost to space.

**Conclusion:** All of the factors at play in the model – crustal production, sputtering, impacts, atmospheric  $\text{CO}_2$  evolution, and erosion – must have affected argon abundances through Mars' history. Moreover, current values represent 4 Gyr of balancing between these processes. At least 67% of  $^{36}\text{Ar}$  must have been lost to space, but the evolution is highly dependent on the chosen sputtering and atmospheric  $\text{CO}_2$  histories and the timing of the disappearance of a global magnetic field. That is, changing these parameters can give rise to different  $^{36}\text{Ar}$  sputtering efficiencies and peak  $^{36}\text{Ar}$  abundances throughout Martian history consistent with present-day values. The SAM instrument measured a present-day  $^{40}\text{Ar}/^{36}\text{Ar}$  of 1900. Due to the amount of argon lost to space in the model, the “re-stored” value of atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  we find is 960 compared to a terrestrial value of 300. This difference could be the result of underestimating early Martian outgassing, late release of  $^{40}\text{Ar}$  from the crust, different formation histories, or other mechanisms not considered. Future measurements by the MAVEN spacecraft of upper atmospheric argon abundances and isotopic ratios will further constrain this model

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