Joint Models for the Evolutionary History of Carbon, Nitrogen, and Argon in the Martian Atmosphere. Trent B. Thomas[1,2], Renyu Hu[2,3], and Daniel Y. Lo[4], [1]Department of Earth and Space Sciences/Astrobiology Program, University of Washington, Seattle, Washington 98195, USA, tbthomas@uw.edu, [2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA, [3]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA, [4]Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA.

Introduction: Morphological and mineralogical evidence indicates that liquid water flowed on ancient Mars's surface (e.g. [1-5]). When considering that Mars's current atmosphere provides little warming and the sun was significantly dimmer in ancient times, a major open question emerges: how was ancient Mars warm enough to allow prolonged liquid water on its surface? One possible answer is warming from greenhouse gases in Mars's atmosphere. To this end, empirical constraints have been placed on the total pressure of the ancient atmosphere. The size distribution of Martian craters suggests a total atmospheric pressure of 0.9 +/- 0.1 bar at 3.5-3.7 Ga, a time when fluvial features were prevalent [6, 7]. Constraints have also been placed on the abundance of individual atmospheric species. Stable isotope analysis indicates an upper bound of 1.8 bar CO_2 at 3.8 Ga [8]. Although CO_2 is a greenhouse gas, it alone cannot generate the necessary surface warming to explain the evidence for liquid water [9]. A recent study has shown that up to 700 mbar N_2 at 3.8 Ga is consistent with fixed-CO_2 isotopic evolution models [10]. A large N_2 reservoir may contribute substantially to surface warming, thus it may help explain the presence of liquid water [11]. Here we present coupled evolutions of atmospheric CO_2, N_2, and Ar that are consistent with the modern-day size and isotopic composition of the Martian atmosphere. Our models indicate that a large CO_2-N_2 atmosphere at 3.8 Ga on Mars is plausible, which has broad implications for potential surface warming.

Model Overview: The numerical model presented here tracks the evolution of both the pressure and isotopic composition ($\delta^{13}C$, $\delta^{15}N$, and $\delta^{38}Ar$) of CO_2, N_2, and Ar in Mars's "free reservoir". The free reservoir includes the atmosphere, regolith, and polar caps. The model starts at 3.8 Ga and evolves to the present by accounting for processes that add, remove, or alter the isotopic composition of each species in the free reservoir. An overview of the model is shown in Fig. 1.

This model includes atmospheric escape via pickup-ion sputtering, photochemical escape of C and N, and ion escape, all of which are impacted by mass-dependent separation above the homopause. Surface processes include addition via volcanic outgassing, and deposition of CO_2 and N_2 as carbonates and nitrates. We also include interplanetary dust particle accretion of Ar and the possibility of the arrival of an Ar-rich comet.

There are several other important aspects of this model: (1) This is the first model to calculate the self-consistent, coupled evolution of CO_2, N_2, and Ar on Mars. The abundance and isotopic composition of each species is calculated at each timestep according to the impact of the sources and sinks. The resulting mixing ratios are then used to adjust the sources and sinks in subsequent timesteps. (2) This model includes the possibility of atmospheric collapse to the poles throughout Mars's history, depending on the total atmospheric pressure and obliquity [12]. (3) We incorporate an updated calculation of the fractionation factor in the photochemical escape of C. (4) We utilize a Markov-Chain Monte Carlo (MCMC) approach to generate probability distributions for model parameter values.

Valid Evolutionary Scenarios: A model run with a given set of parameters and initial abundances is considered a "solution" if the pressure and isotopic composition of each species at the end of the simulation match the present-day measured values to within 3 standard deviations. Through our MCMC analysis of the model parameter space, we have identified over 300,000 solutions. Fig. 2 shows one such solution. In this case, the partial pressures of CO_2, N_2, and Ar at 3.8 Ga are 500, 275, and 1.2 mbar, respectively. The major CO_2 sink is the deposition of carbonate minerals, which is responsible for 430 mbar of loss into the Martian crust. The atmospheric escape of CO_2 via photochemical reactions and sputtering is comparatively small, which is consistent with the low fractionation of modern carbon on Mars ($\delta^{13}C$ = 46 +/- 4‰). This is not the case for N_2, however, as photochemical reactions and sputtering are responsible for 270 mbar of loss to space, which is consistent with the high fractionation of modern nitrogen on Mars ($\delta^{15}N$ = 572 +/- 82‰). Finally, the dominant Ar sink is sputtering, with 0.9 mbar being lost to space. All three species are sourced mainly by volcanic outgassing of volatiles from the Martian mantle. The solutions we've found are consistent with a reduced Martian mantle, with an oxygen fugacity as low as IW-1.

Discussion: These results are significant because they illuminate valid evolutionary trajectories of the

Martian atmosphere. Demonstrating that a potential atmospheric composition and evolutionary history is consistent with modern pressure and isotope constraints, and our knowledge of planetary processes that have shaped Mars, is a valuable method for testing hypotheses about the ancient Martian atmosphere. The solutions that we've found highlight the potential importance of carbonate deposition as a CO_2 sink, the importance of atmospheric escape as an N_2 sink, and the possibility of a reduced Martian mantle.

The solutions we have found show that a CO_2-N_2 rich ancient atmosphere is possible, and that it is consistent with a reduced mantle. This may provide important empirical constraints to solve the early Mars climate problem, as a large N_2 reservoir will enhance CO_2 warming via pressure broadening of absorption lines. Furthermore, the reduced mantle consistent with our evolutionary solutions may lend support to the reducing greenhouse hypothesis, in which reduced gases such as H_2 and CH_4 provide surface warming [13, 14]. For example, a CO_2-N_2-H_2 atmosphere may be an attractive solution, because a large N_2 reservoir would synergistically enhance H_2 warming via collision induced absorption [14]. The results shown here thus present a promising avenue for progress in reconciling Mars's ancient atmospheric composition with geologic evidence for liquid water.

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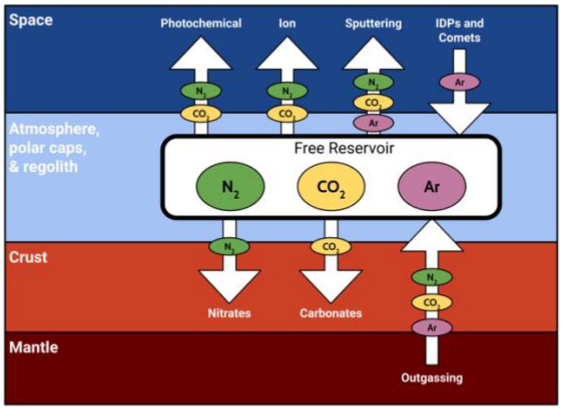

Figure 1: Overview of the box modeling scheme.

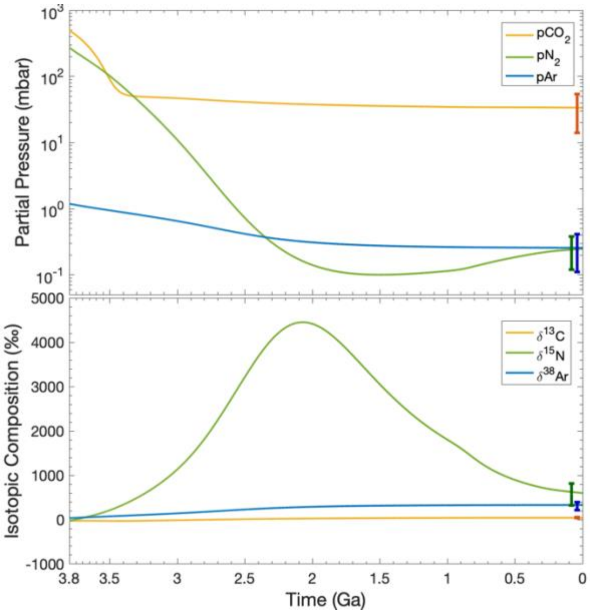

Figure 2: Example of a valid evolution. The brackets represent the modern values in the free reservoir, with 3-sigma uncertainty.