

THE EFFECTS OF DIFFUSION ON OXYGEN ISOTOPES IN THE UPPER ATMOSPHERE OF MARS. M. Brinjikji¹, and J. R. Lyons², ¹Arizona State University, School of Earth and Space Exploration, mbrinjik@asu.edu, ²Arizona State University, School of Earth and Space Exploration, jimlyons2@asu.edu

Introduction: Oxygen isotope ratios have not been fully explored for Solar system atmospheres. One of the main goals of the Mars Atmosphere and Volatile Evolution (MAVEN) spacecraft is understanding how the Martian atmosphere evolved over time; this is accomplished in part by measuring the loss rates of various gases and determining the ratio of stable isotopes in the upper Martian atmosphere [1]. Previous measurements of oxygen isotope ratios in the secondary minerals of Martian SNC meteorites (Fig. 1) show $\Delta^{17}\text{O}$ enrichments of up to ~ 1.3 ‰ (SMOW), suggesting the possibility of modification due to escape of O atoms [2]. We studied similar processes in the upper Earth atmosphere in order to better understand the stable oxygen isotope abundances and the processes that affect them in Earth's thermosphere, specifically possible mass-independent processes such as photodissociation [3]. Now we perform a similar study for the atmosphere of Mars. The main goal of this work is to model the Martian thermospheric O isotope composition using an atmospheric diffusion theory model, and then the more sophisticated VULCAN photochemical code.

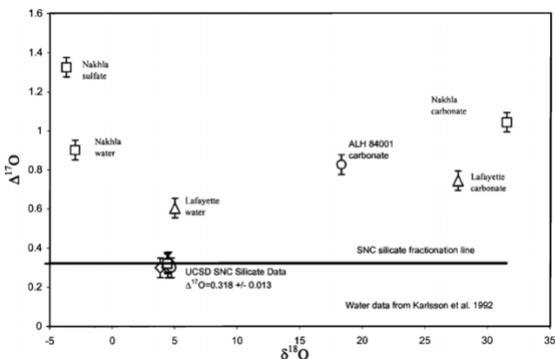


Figure 1. Plot of $\Delta^{17}\text{O}$ vs $\delta^{18}\text{O}$ for secondary minerals in Martian SNC meteorites, from Farquhar and Thiemens 2000 [2].

Atmospheric Structure. The thermosphere of Mars begins at the homopause, which is about 120 kilometers above the surface. The homopause defines the transition between an atmosphere mixed by eddy diffusion (below) and molecular diffusion (above). Above the homopause, heavier species have smaller scale heights than lighter species leading to diffusive separation. Isotope fractionation refers to various processes that change the relative abundances of isotopes. Mass-dependent fractionation (MDF) occurs when the isotope abundance scales with the mass of each isotope. Mass-independent fractionation (MIF) is when the abundance

of the isotopes scales by some other process. We expect that below the homopause there is very little fractionation of isotopes due to eddy diffusion, while above the homopause diffusive separation results in strong mass-dependent fractionation.

To quantitatively describe the effects of isotope fractionation, geochemical ‘delta’ notation is used. Values are given in per mill (‰). For oxygen, the ratio of two stable isotopes relative to a standard is given by $\delta^x\text{O} = 10^3 (R_{\text{sample}}^x / R_{\text{standard}}^x - 1)$ where $R^x = {}^x\text{O} / {}^{16}\text{O}$ for $x = 17$ or 18 . We can compute the quantity $\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda \delta^{18}\text{O}$ (linear approximation) which describes deviation from mass-dependent processes, where λ is typically equal to 0.528. Compounds in Earth’s atmosphere typically have $\Delta^{17}\text{O} = 0$, except when influenced by ozone photochemistry.

Methods: Diffusion Theory Model. In the Martian atmosphere, CO_2 is the most abundant molecule up until very high in the thermosphere, where atomic oxygen becomes an important constituent [4]. From theory [5], the molecular diffusion coefficient (in $\text{cm}^2 \text{s}^{-1}$) for the different oxygen isotope species can be approximated as:

$$D_{12} = 1.96 \cdot 10^6 (1/m_1 + 1/m_2)^{1/2} (T^{1/2}/n)$$

where m_1 and m_2 are the mass of the background air and the mass of the isotope in grams, n is the number density of the background atmosphere approximated as $n = n_i e^{-z/H}$, and H is the scale height of the background atmosphere below the homopause: $H = \frac{kT}{mg}$. The constant in front of the diffusion coefficient is approximated for air on Earth. Due to diffusive separation, the scale height of each oxygen isotope will be slightly different than the scale height of the air below the homopause: $H_i = \frac{kT}{m_i g}$. These components are required for the number density equation:

$$n_x(z) = n_{i,x} \cdot \exp \left[\int_{z_0}^z \left(\frac{1}{H_i} + \frac{1}{H} \frac{K}{D_{12}} \right) \left(1 + \frac{K}{D_{12}} \right)^{-1} dz \right]$$

where $n_{i,x}$ is the number density at the bottom of the atmosphere for isotope x , and K is the eddy diffusion coefficient. For this diffusion theory model of Mars, we used the temperature, eddy diffusion, and number density profiles from Nair et al. 1994 [4]. For altitudes up to 220 km, we calculated the number densities for O, CO_2 and their isotopologues.

VULCAN. We then employed VULCAN, a photochemical kinematics code, for a more accurate look at the number densities of oxygen isotopes in the

upper Earth atmosphere. VULCAN utilizes a realistic temperature profile for Mars and includes chemistry and photochemistry for the most important chemical species in the atmosphere [6]. However, the original version of the code did not include isotopes or ion chemistry, so we modified the code to include both.

Results: Delta values. Figure 1 shows the values for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (‰) calculated using the diffusion theory approximation (solid lines) and VULCAN (dashed lines). We have model results for O and CO₂. The delta values between the two methods are quite similar, only differing by a few per mill. For $\delta^{17}\text{O}$, O is depleted to levels around -150 ‰, while CO₂ is depleted to about -125 ‰ at the top of the atmosphere. For $\delta^{18}\text{O}$, O is depleted to levels around -250 ‰, while CO₂ is depleted to about -225 ‰ at the top of the atmosphere.

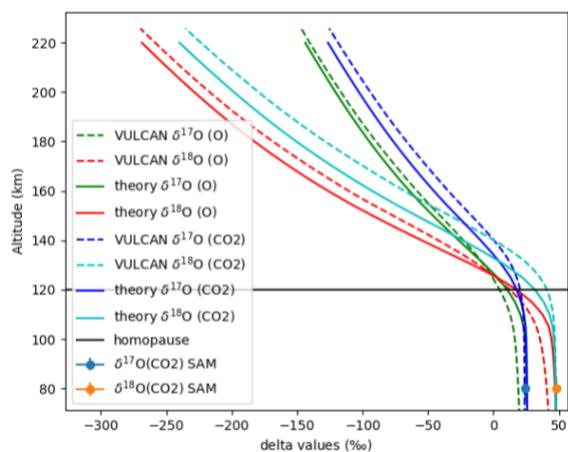


Figure 2. The delta values (‰) for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ calculated from diffusion theory (solid lines) and using VULCAN (dashed lines). The homopause is shown with the solid black line. O is shown in green, O₂ in magenta, and CO₂ in blue. Delta value measurements for CO₂ were taken by the SAM instrument on the Curiosity rover [7].

$\Delta^{17}\text{O}$ plots. Figures 3 and 4 show $\Delta^{17}\text{O}$ from the diffusion theory approximation (solid lines) and VULCAN (dashed lines). Figure 3 shows the behavior of $\Delta^{17}\text{O}$ using the typically-defined slope factor of 0.528. However, this slope factor results in unexpected $\Delta^{17}\text{O}$ enrichments: +8 ‰ for O and CO₂ from the diffusion approximation, and ranging from +4-6 ‰ for the species from VULCAN.

As we did in our Earth study, we redefined the slope factor for $\Delta^{17}\text{O}$ based on the barometric law behavior of the individual isotopes undergoing molecular diffusion: $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.500\delta^{18}\text{O}$ [3]. The results, displayed in Figure 4, show a $\Delta^{17}\text{O}$ enrichment of around +1-2 ‰ for O and CO₂ from the diffusion approximation (solid lines). The CO₂ values from VULCAN (dashed lines) are very slightly positive, while the O and O₂ values are depleted by about 2 per mill.

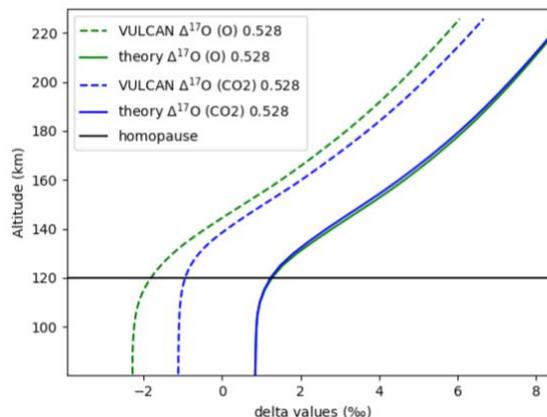


Figure 3. The $\Delta^{17}\text{O}$ values (‰) calculated from diffusion theory (solid lines) and using VULCAN (dashed lines) using the typical slope factor of 0.528.

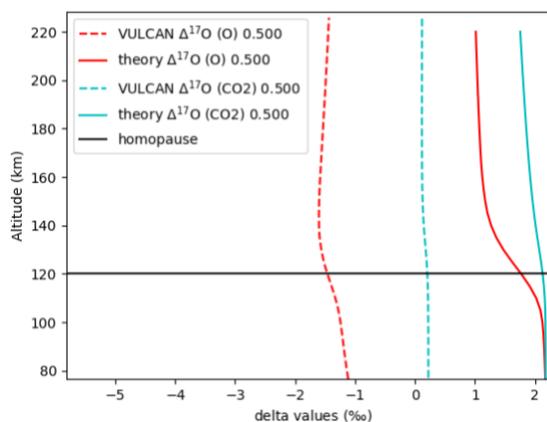


Figure 4. The $\Delta^{17}\text{O}$ values (‰) calculated from diffusion theory (solid lines) and using VULCAN (dashed lines) using a slope factor of 0.500 derived from barometric law behavior.

Conclusions: We find that a fractionation law of 0.500 applies to the thermosphere of Mars in a similar manner as we found for Earth's thermosphere [3]. Because it is likely that Mars lost a significant fraction of its atmosphere due to escape, consistent with estimates of O escape from MAVEN [8], we are now considering the implications of the thermospheric fractionation law to understanding the evolution of O isotopes in Mars volatiles.

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References: [1] B.M. Jakosky et al. (1994) *Icarus*, 111, 2, 271-288. [2] Farquhar and Thieme (2000) *Jour. Geophys. Res.*, 105, E5. [3] M. Brinjkiji and J.R. Lyons (2020) *Rev. Mineral. & Geochem.*, 86, Ch. 6. 197-216. [4] Nair et. al (1994) *Icarus*, 111, 124-150. [5] P.M. Banks and G. Kockarts. (1973) *Aeronomy*, Ch. 15. 32-63. [6] S.M. Tsai et al. (2017) *ApJS*, 228, 2. [7] Webster et al. (2013) *Sci. Reports*, 341, 260-263. [8] Cravens et al. (2017) *Jour. Geophys. Res.*, 112, 1102.