OXYGEN ISOTOPE FRACTIONATION DUE TO NON-THERMAL ESCAPE OF HOT O FROM THE ATMOSPHERE OF MARS. J. R. Lyons[1], [1]School of Earth & Space Exploration, Arizona State University, Tempe, AZ 85281; jimlyons@asu.edu

Introduction: Isotopic analyses of secondary minerals in several SNC meteorites exhibit a mass-independent fractionation (MIF) (i.e., an excess in ^{17}O) in oxygen isotope abundances relative to SNC silicates [1]. Processes that can produce an MIF signature include photodissociation, a few chemical reactions, and possibly other processes such as atmospheric escape [2]. Because O atoms escape from Mars as a result of dissociative recombination of the predominant ionospheric ion, O_2^+, which imparts excess kinetic energy to the resulting neutral O atoms [3], [4], it is possible that O escape over time has modified the O isotope composition of Martian volatiles.

To address the possibility that escape is responsible for the MIF signature in Martian volatiles, I use a Rayleigh distillation model. However, rather than applying this model from the homopause to the exobase, as is usually done, I apply it from the homopause to the escape altitude of hot O atoms, which is generally below the usually defined exobase. Additionally, because there is evidence from MAVEN observations for variation in the altitude of the homopause [5], I consider how O isotope ratios in the non-escaping fraction of the atmosphere could vary as a function of homopause altitude.

Mars atmosphere: I use the temperature, number density and eddy diffusion coefficient profiles from the baseline model of Nair et al. [6]. The homopause, the altitude at which eddy and molecular diffusion coefficients are roughly equal, occurs at about 120 km in that model. Above the homopause diffusive separation causes a depletion of the heavier isotopes [7]. Escape of O*, a hot O atom produced by $O_2^+ + e \rightarrow O^* + O^*$, occurs down to about 175 km according to Monte Carlo simulations [8]. I also consider escape from 145 km as a lower limit for simpler collisional estimates of hot O escape [9]. Homopause altitude has been inferred to vary from about 70 to 125 km from measurements of number densities in MAVEN NGIMS data [5]. The exobase altitude is observed to be roughly correlated with homopause altitude, suggesting contract and inflation of the entire upper atmosphere perhaps due to varying degrees of gravity wave dissipation.

Rayleigh distillation model: Rayleigh distillation describes isotopic fractionation in a well-mixed system as material moves between 2 reservoirs, in this case material lost to space and the fraction of retained atmosphere. To be applicable to the upper atmosphere of Mars, the timescale for molecular diffusion must be shorter than the loss timescale for loss of O from the upper atmosphere. This can be shown to be valid for O above the homopause for the conditions considered here. The Rayleigh distillation equation is $R = R_0 f^{\alpha - 1}$ where R is the ratio of heavy to light isotope in the atmosphere, f is the fraction of atmosphere remaining, and α is the fractionation factor. The fractionation factor at altitude z is the ratio of ^{x}O/^{16}O at z divided by the same ratio at z_h, the homopause altitude,

$$\alpha_x = e^{-(z - z_h) GM \Delta m_x / r^2 kT}$$

GM/r^2 is local gravity at $r = R_{Mars} + z$ and $\Delta m_x = m_x - m_{16}$ for x = 17 or 18. Fractionation factors are plotted in Figure 1.

Results: The O isotopic ratios of the atmosphere expressed as delta-values are given in Figures 2 and 3 as a function of the fraction of atmosphere remaining. I have assumed a starting isotopic composition of SMOW for Martian volatiles. This assumption is clearly open to debate, but it provides a convenient reference point for illustrating the effects of atmospheric loss within the Rayleigh model. For O escape at 175 km, enrichment comparable to the observed δ-values for CO_2 near the Martian surface (gray bars, Fig. 2a, [10]) requires loss of 15 – 30% of the atmosphere for homopause altitudes from 70 – 125 km, respectively. Enrichment of Δ^{17}O from a SMOW value of zero to about 0.8 ‰, a typical value from SNC secondary minerals (gray bar, Fig. 2b, [1]) requires loss of about 15% of the atmosphere for a homopause at z_h = 70 km, and 75% loss for z_h = 100 km. For the homopause at 125 km, a depletion occurs for z_h = 125 km, so agreement with the SNC data is not possible. A homopause altitude of 70 km yields consistent enriched values for δ^{17}O, δ^{18}O and Δ^{17}O for O escape from 175 km. For O escape from 145 km, the solutions are more divergent with atmospheric loss spanning 15 – 45% for z_h = 70 – 125 km (Fig. 3) for δ^{17}O and δ^{18}O, and a loss of 20% for z_h = 70 km for Δ^{17}O. Depletions in Δ^{17}O are predicted for z_h = 100 and 125 km (not shown). Again, the most consistent solution is for a quite deep homopause altitude of 70 km. The loss of about 20% of O predicted from this model is lower than the 66% loss of atmospheric Ar derived from MAVEN measurements of ^{38}Ar/^{36}Ar [11].

Conclusions: Using a Rayleigh distillation model and O escape altitudes below the exobase, I have shown that O isotope ratios consistent with modern atmosphere CO_2 and SNC secondary minerals occur for ~ 20% oxygen loss from the atmosphere and for a homopause altitude of ~70 km. This result assumes initial isotope ratios similar to SMOW. Evolution models that include early high solar EUV are the next step to fully address the evolution of O isotope ratios.

References: [1] J. Farquhar and M. Thiemens (2000) *JGR*, *105*, E5. [2] B. Jakosky (1993) *GRL*, *20*, 1591-1594. [3] J. Fox and A. Hac (2010) *Icarus*, *208*, 176-191. [4] B. Jakosky et al. (2018) *Icarus*, *315*, 146-157. [5] M. Slipski et al. (2018) *JGR Planets*, 123, 2939-2957. [6] H. Nair et. al (1994) *Icarus*, *111*, 124-150. [7] M. Brinjikji and J. Lyons (2021) LPSC 52^{nd}, abstract #2544. [8] A. Rahmati (2016) PhD thesis, Univ. Kansas. [9] T. Cravens et al. (2014) *JGR*, *112*, 1102. [10] C. Webster et al. (2013) *Science*, *341*, 260-263. [11] B. Jakosky et al. (2017), *Science*, *355*, 1408-1410.

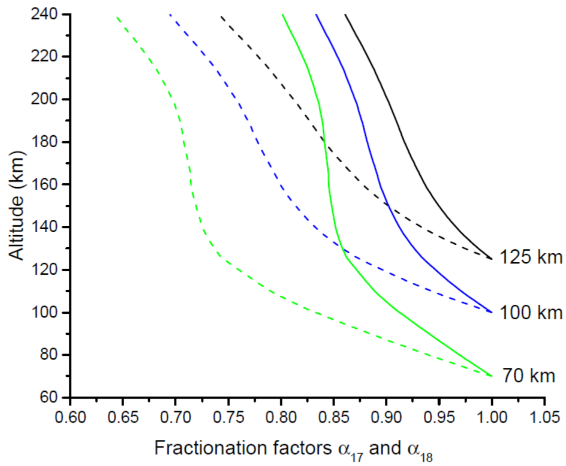

Figure 1. Fractionation factors for ^{17}O (solid) and ^{18}O (dashed) for 3 model homopause altitudes of 70, 100, and 125 km.

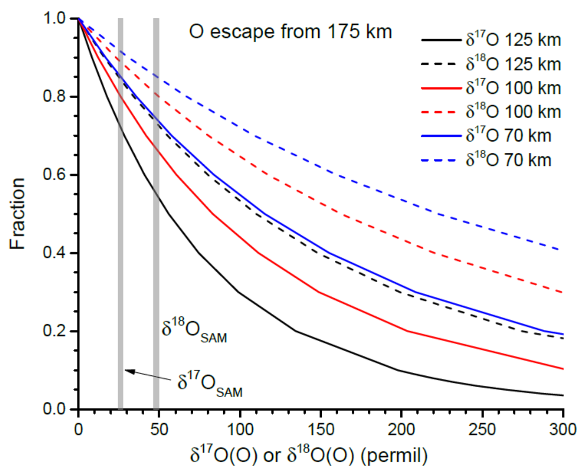

Figure 2a. Delta-values for the remaining fraction of bulk atmosphere oxygen assuming hot O escape from an altitude of 175 km. Three homopause altitudes are considered, 70, 100 and 125 km. The vertical gray bars are the $\delta^{17}O$ and $\delta^{18}O$ values for CO_2 measured by the SAM instruments on the Curiosity rover [10].

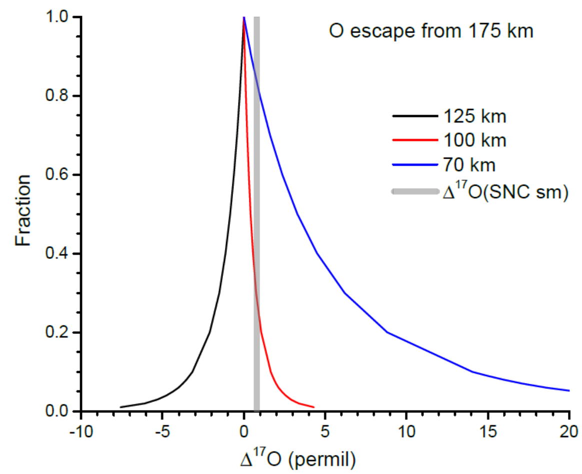

Figure 2b. The corresponding mass-independent delta-value, $\Delta^{17}O$, for O escape from 175 km. A fractionation law exponent of 0.528 is used. The vertical gray bar is the approximate enrichment seen in SNC secondary minerals (sm), including carbonates and water [1].

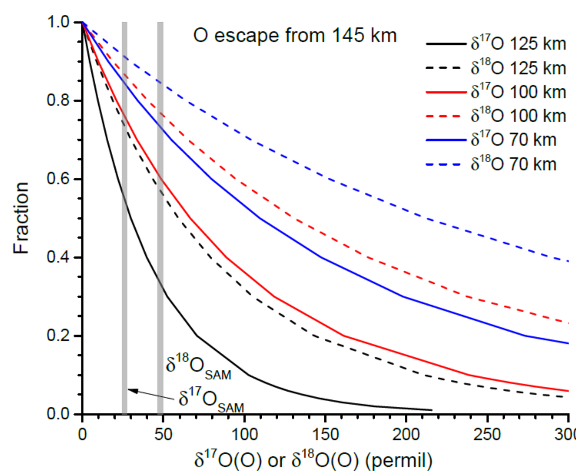

Figure 3. Same as Figure 2a but for O escape at 145 km.