



RESEARCH LETTER

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Nitrogen Fixation at Paleo-Mars in an Icy Atmosphere

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Key Points:

- In a cold climate, heterogeneous reactions with atmospheric ice particles would cause faster deposition of HNO_x than dry deposition
- Formation of HNO_x species is faster for earlier Martian climates of larger surface pressure
- Modeled NO accumulates to amounts greater than present-day measurements, so we propose there may be a loss mechanism that is unidentified

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Recent findings of NO near Gale Crater on Mars have been explained by two pathways: formation of nitric acid (HNO₃) in a warm climate or formation of peroxyntic acid (HO₂NO₂) in a cool climate. Here, we put forth two hitherto unexplored pathways: (a) deposition of nitric/peroxyntic acid onto ice particles in a cold atmosphere, which settle quickly onto Mars' surface and (b) solar energetic particle-induced production of nitric/peroxyntic acid. The deposition rates are enhanced and NO production is more efficient under the higher atmospheric pressures typical of Mars' ancient atmosphere. Depending on the unknown rate at which nitric/peroxyntic acid is lost from the surface, the new pathways could result in larger NO-levels than those detected by the Mars Science Laboratory. We predict a 2:1 ratio of nitrite:nitrate would have deposited in cool surface climates with an icy atmosphere, whereas orders of magnitude more nitrate than nitrite is expected from warm surface climates.

Plain Language Summary The nitrogen oxides discovered in present-day soil on Mars likely formed in the atmosphere before being deposited on the ground. Two possible mechanisms are deposition of nitric acid (HNO₃) when Mars had a warm climate and deposition of peroxyntic acid (HO₂NO₂) during cold climate. The latter scenario involves processes that have not been considered previously and leads to a much faster deposition rate for nitrogen oxides than was reported in previous studies: solar energetic particles splitting N₂ in the middle atmosphere, reactions of nitrogen oxides on the surfaces of ice particles in the atmosphere, and deposition of peroxyntic acid onto the Martian surface when surface pressure was higher. Depending on the unknown rate at which they are lost from the surface due to UV photolysis, the maximum accumulation rate for nitrogen oxides could be much larger than is required to explain the present day measurements. We predict that more nitrite would form than nitrate in a cool climate with an icy atmosphere, whereas in a warm climate much more nitrate than nitrite is expected. So, an investigation of the relative amounts of NO₂:NO₃ in the soil in the present-day measurements could reveal the climate state under which the salts formed.

1. Introduction

Evolved gas analysis measurements of Mars' soils made by the Sample Analysis at Mars (SAM) instrument on board the Mars Science Laboratory (MSL) recently discovered 70–260 and 330–1,100 ppm of NO in the Klein and Cumberland Noachian-aged mudstone deposits, respectively, at Yellowknife Bay (Stern et al., 2015). Subsequent measurements of 0.002–0.05 wt% of NO in sediments near Gale Crater were also reported (Sutter et al., 2017). The presence of NO suggests a nitrogen cycle during Mars' history. This would be relevant to astrobiology, as nitrogen fixation is required for nitrogen to be useful to terrestrial life (e.g., Holm & Neubeck, 2009; Mancinelli & McKay, 1988). However, the precise mechanism of the nitrogen cycle on early Mars remains debated.

Adams et al. (2021) showed that the observed nitrates could have been formed by lightning-induced nitrogen fixation if the Mars climate was predominantly warm and wet throughout the history (~3 Ga). However, geochemical and geomorphological evidence suggests that the warm wet climate might be only episodic of 10⁵–10⁷ years duration (e.g., Barnhart et al., 2009; Carr & Head, 2003; Clifford & Parker, 2001; Grotzinger et al., 2015; Hoke et al., 2011). The present-day abundance of ancient olivine and the relative lack of surface carbonates suggest a wet climate was likely not present for up to ~millions of years (e.g., Ehlmann & Edwards et al., 2014; Olsen & Rimstidt, 2007). Recent works further suggest that climate warming mechanisms likely only

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allow the climate to have been warm and wet for brief windows of Mars' history during the Noachian and early Hesperian. Some suggest that episodically released H₂ (from volcanism or impacts) in a CO₂ atmosphere could cause temporary warming (e.g., Wordsworth et al., 2021). Otherwise, the climate has likely been cold, as a CO₂ atmosphere alone, without trace amounts of H₂ or CH₄, does not provide sufficient greenhouse warming (Kasting et al., 1991; Wordsworth et al., 2017). For the most recent ~3 Ga, a thinning atmosphere would have kept the post-Hesperian relatively cool (e.g., Wordsworth, 2016; Hu et al., 2015).

Therefore, HNO_x deposition could have occurred under several scenarios: (a) a warm surface with liquid water; (b) a cool surface; (c) a hybrid of (a) and (b). Regardless of whether ice is present on the surface, ice is expected in the atmosphere of a cool climate (and potentially high in the atmosphere of a warm climate, like Earth's). Even during cold climates, early Mars likely had large inventories of water (e.g., Jakosky & Hallis, 2024) and at present day water remains in the atmosphere as vapor (e.g., Fischer et al., 2019) and ice (e.g., Kleinboehl et al., 2009), which is in exchange with water ice at the polar caps (e.g., Titov et al., 2002). In cool climates, the surface ice (e.g., at the caps) and the atmospheric water vapor would have been near equilibrium. Atmosphere-surface exchange through, for example, deep convection, would also naturally result in ice particles in the upper troposphere of Mars.

Mancinelli (1996) predicted that the formation of nitrates at early Mars in cool climates would arise via the formation of odd nitrogen radicals from the photodissociation of N₂ and ion-neutral reactions in the thermosphere, which, upon transporting downwards, may be oxidized to form nitric acid (e.g., Krasnopolsky, 1993; Yung et al., 1977). Catling et al. (2013) and Smith et al. (2014) also considered formation and dry deposition of peroxy-nitric and nitric acid in 7- and 35-mbar Amazonian atmospheres. They found that dry deposition of the former exceeded the latter by two orders of magnitude and N accumulation during the Amazonian of 0.4–0.2 wt% if mixed uniformly to a depth of 1.5–2.6 m. These studies can explain the MSL data, but their HNO_x deposition could be a lower bound, as we will show in this work. We add modeling details to bring the models closer to reality by: (a) including interactions with ice particles in the middle atmosphere; (b) considering larger atmospheric pressures for earlier periods of Mars' history; and (c) considering solar energetic particles (SEPs) in the thermosphere.

2. Methods

We adapt KINETICS, the Caltech/JPL chemical transport model (e.g., Allen et al., 1981), to a 1D and diurnally averaged present-day Mars environment as in Nair et al. (1994). KINETICS has been applied to and validated against data for many other worlds (e.g., Li et al., 2014; Moses et al., 2005; Wong et al., 2015), including nitrogen fixation in warmer climates for the early Earth (Wong et al., 2017) and for early Mars (Adams et al., 2021).

We investigate icy nitrate formation under five atmospheric pressures: 7 mbar, 50 mbar, 200 mbar, 500 mbar, and 1 bar. The reaction rates are listed in Table S1 in Supporting Information S1, and the species, boundary conditions, and model assumptions are in Text S3 in Supporting Information S1. We use mixing ratios of N₂ and CO₂ of 2.7% and 97.3% for present-day conditions (Trainer et al., 2019) and 10% and 90% for thicker atmospheres (Hu & Thomas, 2022). A dry deposition velocity of 0.02 cm s⁻¹ for nitrous, nitric, and peroxy-nitric acid is considered (Krasnopolsky, 1993; Smith et al., 2014), along with an upper boundary flux of N and N(²D) to account for SEP deposition (Adams et al., 2021). Solar spectrum changes over time are parametrized according to Claire et al. (2012), assigning 3.8 Ga flux for 500- and 1000-mbar cases, 2.7 Ga for 50- and 200-mbar cases, and present-day flux for the 7-mbar case.

Water ice amounts are based on Mars Climate Sounder (MCS) measurements from Mars years 29–33, averaged over specific periods (Kleinböhl et al., 2009, 2017). Ice particle properties are derived using a particle size distribution with an effective radius of 1.41 μm (Kleinböhl et al., 2011). The rate coefficient for loss through reactions on ice aerosols is given by:

$$J_{ice} = \frac{1}{4} \gamma \nu \sigma N_{ice} \text{ (unit : s}^{-1}\text{)} \quad (1)$$

where γ is the sticking coefficient (with a value of 0.01 from Michelangeli et al., 1989), ν is the gas's thermal velocity, σ is the ice particle's cross-sectional area, and N_{ice} is the ice particle number density (Yung & Demore, 1982). The computed time-averaged J_{ice} profile is plotted in Figure S1 in Supporting Information S1.

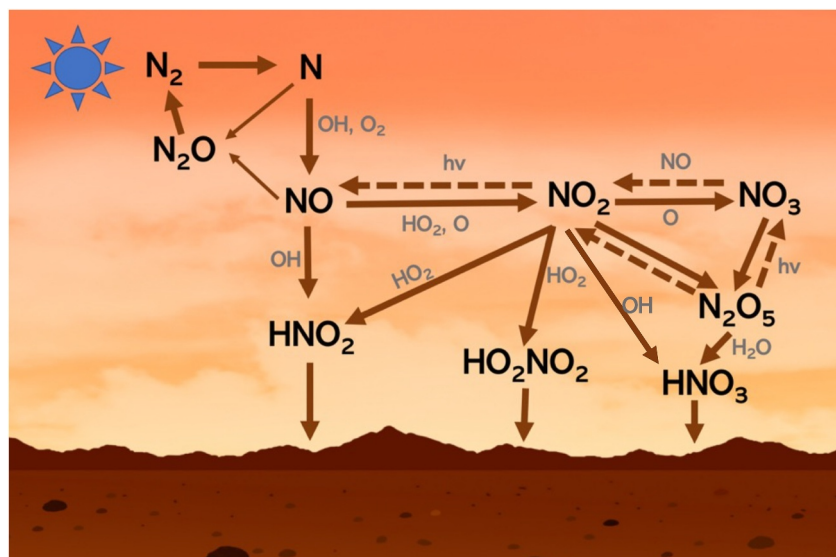


Figure 1. Cartoon of the relevant odd-nitrogen chemistry in Mars' atmosphere. N_2 dissociation by solar energetic particles causes NO formation, oxidation of which leads to HNO_x production and deposition.

Earlier atmospheres likely had higher ice concentrations; thus, we scale present-day ice concentrations by factors of 1 \times , 3 \times , and 10 \times for all scenarios. A 0 \times case is also shown in Figure 3 for comparison with previous studies (e.g., Smith et al., 2014).

The rate of N_2 destruction by SEPs is adopted from Nair et al. (1994), and incident EUV flux parametrized for early Mars according to Claire et al. (2012).

3. Results

3.1. Photochemical Production of Nitric and Nitrous Acid

Nitrous acid (HNO_2) and peroxyntitric acid (HO_2NO_2 or HNO_4) in Mars' atmosphere are produced from a chain of reactions involving the odd-nitrogen (NO_x) species. Formation of HNO_x first requires an energy input to break the strong triple bond of N_2 . Dissociation by SEPs is faster than photolysis. Oxidation of the products forms NO, and NO may directly produce HNO_2 through reacting with OH, or it may produce the other NO_x species through reactions with O and HO_2 . Some NO may also react with N to form N_2O , and which often cycles the fixed-N back to N_2 through photolysis and reactions with $O(^1D)$. N_2O reacting with $O(^1D)$ may also form two NO molecules. NO_2 contributes to formation of both nitrous acid and peroxyntitric acid through reactions with HO_2 , and in a self-terminating reaction the NO_x species NO_2 and NO_3 form N_2O_5 . NO_3 and N_2O_5 are both generally susceptible to destruction by photolysis. N_2O_5 may also react with water vapor or on the surface of water ice particles to produce nitric acid (HNO_3). The HNO_x species may then be absorbed onto ice particles and deposited directly to the surface. These chemical pathways are summarized in Figure 1.

The steady-state mixing ratios which result from the above chemistry are shown in Figure 2. The energy deposited and thereby the rate of N_2 destruction is the same in all climate scenarios, causing N and NO mixing ratios to become smaller in the denser atmospheres. In the thicker atmospheres, collisions are more frequent, causing the availability of N to become limited to higher altitudes only. Similarly, the NO profile (sourced by N) tends to curve back to lower values near the surface in the atmospheres of higher surface pressure. The availability of NO decreases slower than that of N due to both a greater availability of HO_x in the thicker atmospheric cases (since its production rate scales with the concentrations of both N and the oxidant) and the additional source of NO from N_2O photolysis. Thus, the mixing ratios of HNO_x are more consistent across the different atmospheric densities than the nitrogen species. For example, in the case of the lowest ice concentration (solid pink lines), the near-surface HO_2NO_2 is near $\sim 10^{-12}$ (within a factor of ~ 3) for all atmospheric pressures. However, in the cases with more ice in the 200-mbar atmosphere, the limited availability of lower atmosphere N and NO causes much smaller near-surface mixing ratios of HNO_x species. The ice content not only removes HNO_x faster but also H_2O_2

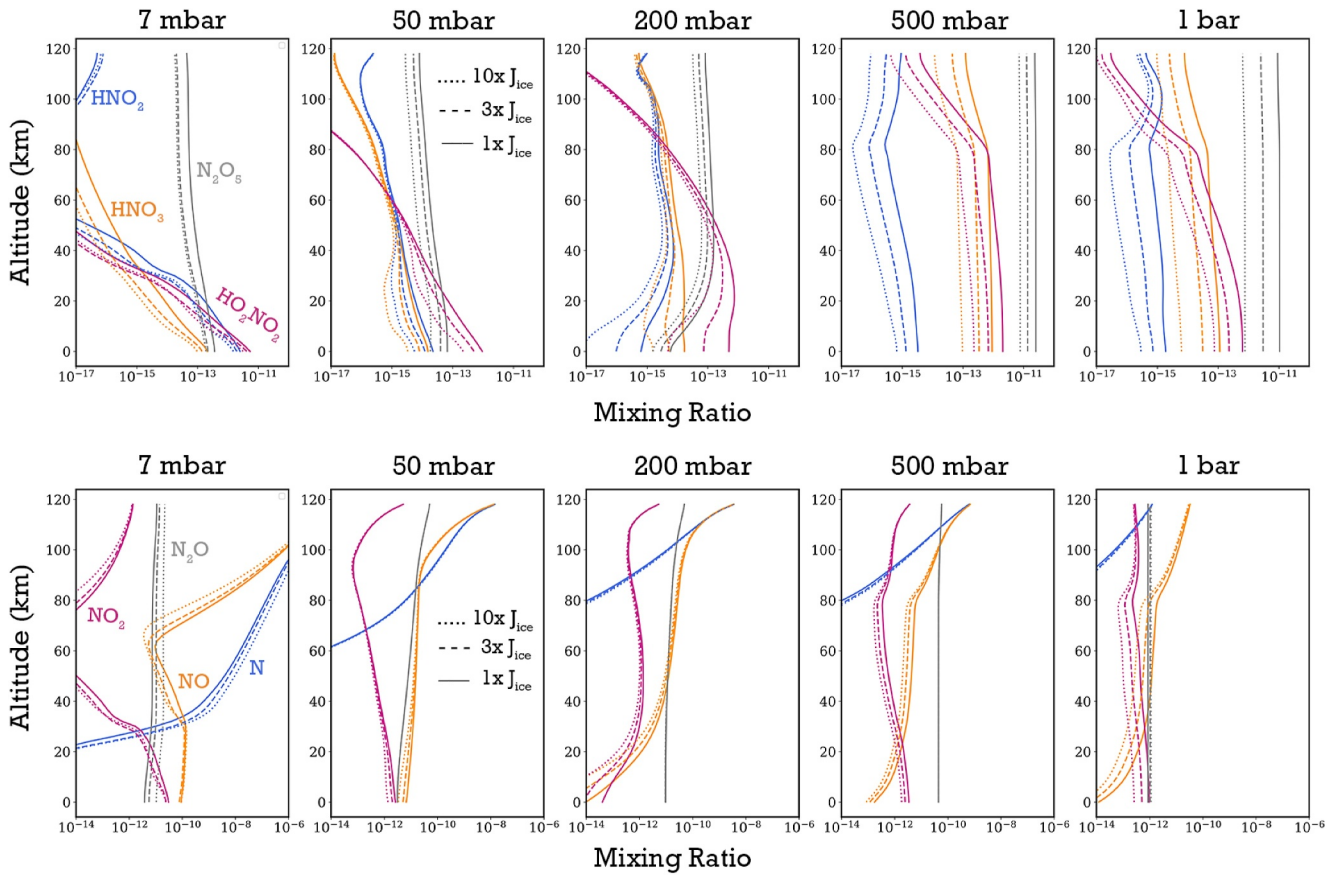


Figure 2. Mixing ratios of nitrous acid (blue), nitric acid (orange), peroxyntic acid (magenta), and N_2O_5 (gray) are shown in the upper panels. Mixing ratios of N (blue), NO (orange), NO_2 (magenta), and N_2O (gray) are shown in the lower panels. Five climate scenarios are considered from left to right: 7 mbar, 50 mbar, 200 mbar, 500 mbar, and 1 bar. In each panel, the ice concentration is varied from $1\times$ (solid), $3\times$ (dashed), and $10\times$ (dotted) the temporal average from Mars Climate Sounder data as described in Figure S1 in Supporting Information S1.

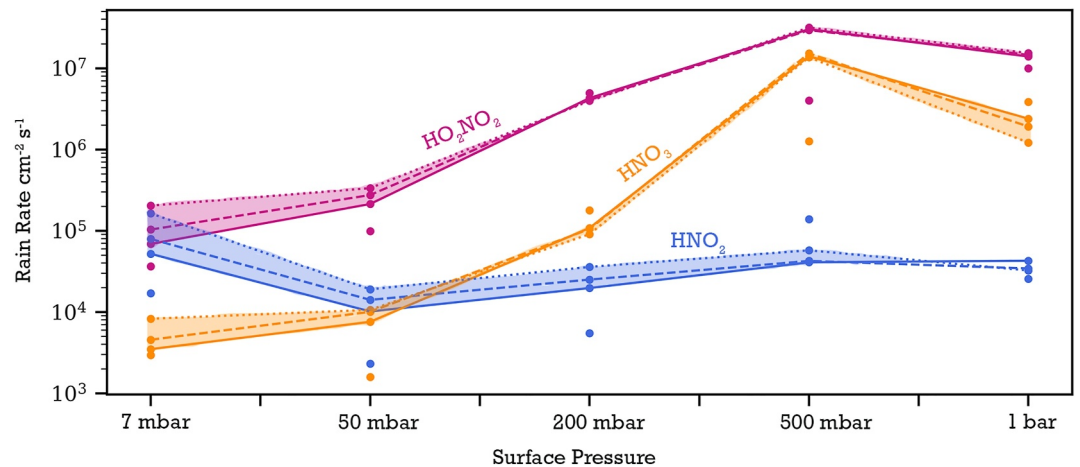


Figure 3. Rate of deposition of HNO_x species on ice particles to the Mars surface ($cm^{-2} s^{-1}$) in five climate scenarios: 7 mbar, 50 mbar, 200 mbar, 500 mbar, and 1 bar. Cases with no ice particles (i.e., the $0\times$ case) are shown in the unconnected dots. Cases with ice particles are shown for each value of f : $1\times$ in solid, $3\times$ in dashed, $10\times$ in dots.

and HO₂, which influences the redox state of the atmosphere and slows the reactions which oxidize N and NO. Additionally, in thinner atmospheric cases, the lower density and constant destruction rate of N₂ makes NO more likely to collide and react with N, which forms N₂O and ultimately recycles the NO_y species back to N₂. Therefore, in thicker atmospheric cases, a greater fraction of the produced NO will go on to form nitrous and nitric acid. The formation of nitric acid requires reactions with water vapor, and the thicker atmospheric cases foster greater saturation vapor pressures of water. (The water vapor also extends to higher altitudes in the cases of higher pressure, but this is less significant since the N- and NO_x-availability also become more limited to higher altitudes in these cases due to more frequent collisions.) Therefore, the steady-state mixing ratios of nitric acid are greater in the 500-mbar case than the 50- and 200-mbar cases.

The cases with greater ice abundances result in faster loss of HNO_x and N₂O₅, partially due to the adsorption onto the particles and reactions with the ice particle surfaces, respectively. The larger ice abundance also causes faster removal of H₂O₂, causing a decrease in OH and atmospheric oxidants. This causes a small increase in N and contributes to slower production of NO and HNO_x species, which are largely produced through reactions with HO_x.

3.2. Deposition Rate of HNO_x on Ice Particles

We find that deposition of HO₂NO₂ generally dominates the flux of HNO_x species to Mars' surface in icy climates, as summarized in Figure 3. This differs from terrestrial chemistry, where nitric acid deposition is faster than that of peroxyntic acid because of rapid thermal decomposition in the lower troposphere; however, this rate has a strong temperature dependence and is orders of magnitude slower from tens of degrees of cooling (Gierczak et al., 2005; Graham et al., 1978). The rate of thermal decomposition of HO₂NO₂ in the cool 1-bar early Mars atmosphere is slower than photolysis at the surface by more than two orders of magnitude at 200 K and by ~4 orders of magnitude at 180 K. A similar temperature-dependence for present-day Mars' peroxyntic acid formation was discussed in Catling et al. (2013), with reference to present-day Mars and terrestrial processes (Gierczak et al., 2005; Graham et al., 1978; Slusher et al., 2002). HO₂NO₂ is formed fastest in the thicker atmosphere cases due to a pressure dependence of the rate for its main production pathway: HO₂ + NO₂ + M → HO₂NO₂ + M. In contrast, the formation of nitric acid at early Mars occurs through several reactions, all of which are slower than peroxyntic acid production: In the thicker atmospheres, N₂O₅ may react with water to form nitric acid, but this reaction is primarily limited to the lowest ~20 km, where water vapor concentrations are largest. In the thin atmospheres, both water vapor and N₂O₅ abundances are low and instead, production of HNO₃ near the surface requires that NO₃ become oxidized by HO₂; however, the NO₃ concentrations are smaller than NO₂ by several orders of magnitudes (thereby again favoring peroxyntic acid over nitric acid formation). In all cases, nitric acid production in the relatively dry upper atmosphere is limited to oxidation of NO₂ by OH, but, like other HNO_x species, the near-surface production is faster.

The deposition rates of both peroxyntic and nitric acid to the surface largely increase as the atmospheric pressure increases. Loss of all HNO_x species is primarily by photolysis, which is much faster than loss to ice particles; however, photolysis rates are relatively consistent between the 50-, 200-, and 500-mbar cases (see Figure 4). Therefore, this trend in deposition rates must be driven by the production rates. HO₂NO₂ is primarily formed when HO₂ attacks NO₂, and this reaction occurs ~10× faster in the 500-mbar case than in the 50-mbar case (see Figure 4), primarily due to a pressure-dependence of the termolecular reaction: HO₂ + NO₂ + M. The concentration of NO₂ also influences this rate. NO₂ is larger in the thicker atmospheres (500 mbar and 1 bar) due to greater amounts of O₃ available to oxidize NO to NO₂ compared to the thinner cases (7 and 50 mbar). However, the 200-mbar case sees a depletion in NO₂ due to a limited availability of HO_x in the upper atmosphere, which limits conversion from N to NO. This may be due to a larger CO abundance, where the greater CO₂ photolysis rate depletes the upper atmosphere of oxidants in order to convert CO back to CO₂. The production of nitric acid is faster in the thicker atmospheres largely due to the reaction N₂O₅ + H₂O becoming the dominant pathway (see Figure 4). This is attributed to a greater availability of surface liquid water (directly caused by the greater pressures) and of N₂O₅. The near-surface N₂O₅ concentration increases with surface pressure with a notable transition occurring between the 200-mbar and 500-mbar cases. The greater NO₂ concentrations facilitate faster formation of NO₃, both of which increase the rate of N₂O₅ production.

We approximate to an order of magnitude the concentration of salts that have accumulated in the Mars soil: We attempt to estimate the duration of each of our four surface pressures by discretizing the rate of atmospheric CO₂

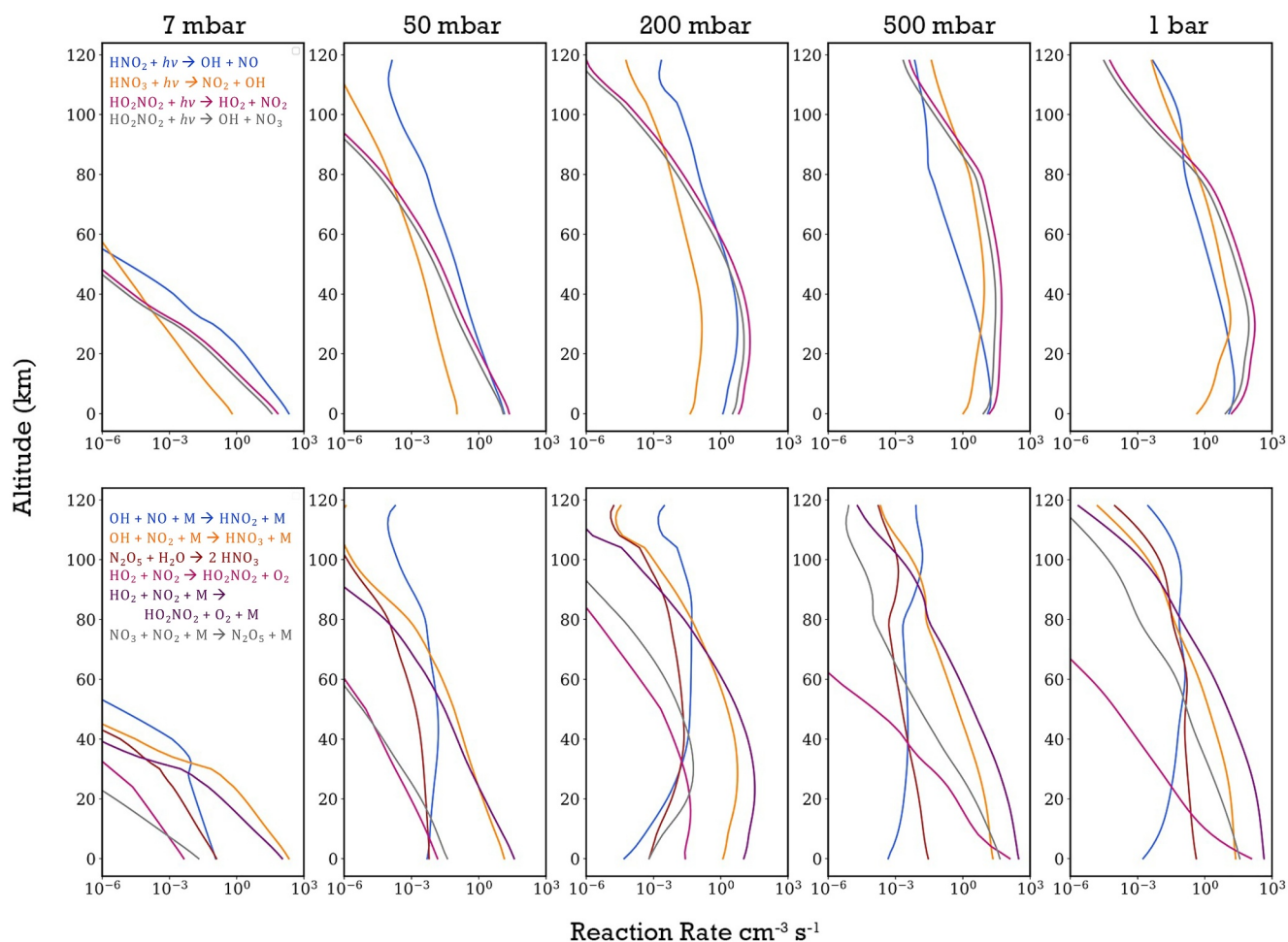


Figure 4. Reaction rates ($\text{cm}^{-3} \text{s}^{-1}$) for loss by photolysis (upper panel) and production (lower panel) reactions for HNO_x species. Different climate scenarios are shown in panels from left to right: 7, 50, 200, 500, and 1 bar. For clarity within each panel, only the $1 \times J_{\text{ice}}$ case is shown.

loss described in Hu et al. (2015) and extrapolating back to 4.1 Ga (the start of the Noachian); although we acknowledge these are highly uncertain and that the surface pressure would have likely decreased more smoothly over time: ~ 300 Ma each in the 1-bar, 500-mbar, 200-mbar, and 50-mbar climates and the remainder of Mars' history (~ 3 Ga) in the 7-mbar climate. From this, we find that most nitrite and nitrate deposition occurs during the 1-bar and 500-mbar climates. Following deposition on ice and settling of the ice to the surface, we assume the soils are mixed throughout a shallow depth due to post-Noachian impactors. We consider ~ 2 m, which represents three e -folding depths (Zent, 1998). We also assume a soil density of 1 g cc^{-1} (Moore & Jakosky, 1989). These assumptions are consistent with those in Smith et al. (2014). We assume that the loss rates of nitrate and nitrite following deposition are negligible. Nitrates in ice cores are thought to be long-lived and have been used as proxies at Earth for studying the occurrence of past SEP events (Dreschhoff & Zeller, 1990; Schrijver et al., 2012). However, the extent to which we can ignore loss after deposition requires future study, both laboratory and modeling. On Earth, nitrate in ice and snow can return to the atmosphere as $\text{HNO}_3(\text{g})$ before being deposited again. Evidence for such a cycle from snow to atmosphere (Zatko et al., 2016) has been identified in the $\delta^{15}\text{N}$ snow and ice core nitrate (Akers et al., 2022; Erbland et al., 2013; Jiang et al., 2021). Conditions on Mars (variable mixture of CO_2 - H_2O ice, different atmospheric composition) could lead to significantly different photolysis rates for deposited nitrites and nitrates than has been found on Earth. To our knowledge, no such study of Mars through geologic time has been carried out and would be worth further investigation. We assume that no aqueous systems existed during this part of Mars' history, although episodic warm climates, and hence transient aqueous conditions, might have existed on Mars throughout its history (Wordsworth et al., 2021), in which new loss

mechanisms including photoreduction, loss to iron, and hydrolysis could have been invoked (Ranjan et al., 2019; Wong et al., 2017). Under these assumptions, our 1× ice case's deposition fluxes correspond to the weight percents of ~4 wt% NO from nitrate and ~8 wt% NO from nitrite. These are much greater than the MSL findings (70–1,100 ppm; Sutter et al., 2017; Stern et al., 2015), suggesting that nitrate and nitrite were likely altered on Mars' surface and lost over time through a currently unidentified surface process (such as cosmic rays). We urge for future investigation of surface loss processes for surface nitrate in cold climates or a better constraint of the occurrence and duration of short aqueous episodes at Mars through time.

3.3. Uncertainty Estimation of Surface NO Budget

Any assumption of a persistent warm or cool surface climate throughout the Mars history is likely unrealistic. An uncertainty of N in soil is associated with the duration of the warm and cool eras. Wordsworth et al. (2021) suggest the climate (earlier with a thicker atmosphere, like our 1 bar case) may have alternated between warm and cold climates, but also demonstrate that surface liquid water after 3 Ga is unlikely due to cool surface temperatures. In warm scenarios, loss to photoreduction would be particularly fast ($\tau \sim 1$ year; Mack & Bolton, 1999). Our estimated weight percents (~4% NO in nitrate, 8% NO in nitrite) may be subject to an uncertainty due to the uncertainty in the duration of warm versus cool periods in Mars' history. Ignoring all nitrite and nitrate deposition in the 1 bar atm (considering warm climates may have intermittently occurred under this climate regime) would decrease our estimations by a factor of ~2. Nonetheless, ~4 wt% NO in nitrite is still ~40× larger than present-day measurements and suggests an unidentified loss. This lower estimate is also ~10× larger than the estimates in Smith et al. (2014).

4. Discussion: Interpreting the Formation of MSL-Measured Volatiles

We find that icy climates form and deposit peroxyntic acid fast enough to produce global-average nitrate deposits much larger than the MSL-measurements. Although we acknowledge that the MSL measurements may not be globally representative (e.g., ices and/or NO_x could transport to locally collect in some regions), we propose an unidentified loss mechanism for surface NO-salts in the Mars soils could improve model-data comparisons. There are also limitations in photochemical modeling which could contribute to uncertainty, including reaction rates which may be estimated from the combustion literature and not at Mars-like temperatures.

Our result does not rule out the formation of nitrates in warm and wet climates (e.g., Adams et al., 2021). However, it suggests the nitrates measured by MSL could be formed by two mechanisms at different epochs in time. Future measurements of N-isotopes in the Martian nitrates could help constrain when the nitrates formed. Over Mars' history, the atmospheric isotopic record became enriched in heavy isotopes due to atmospheric loss to space; since nitrate formation originates with atmospheric chemistry under both regimes, nitrates formed during the warm and wet climate would likely be older and thus of lighter isotopic signatures than nitrates formed during the cool, icy climate. Surface loss processes (such as photoreduction in the warm, wet climates) may also influence the abundance of nitrates and nitrites, as well as ¹⁴N/¹⁵N.

Catling et al. (2013) and Smith et al. (2014) showed that peroxyntic acid deposition may occur faster than nitric acid. Our model further enhances the peroxyntic deposition via reactions on the surfaces of ice particles. We found a surface pressure dependence on total HNO_x rainout rates and the relative rates of peroxyntic versus nitric acid. Integration over time periods predicts a ~2:1 nitrite:nitrate ratio from HNO_x deposition in cold climates. The fate of peroxyntic acid on deposition could result in surface nitrite salts (Catling et al., 2013; Regimbal & Mozurkewich, 1997; Slusher et al., 2002), contrasting with warm climates that produce significantly more nitrate (Adams et al., 2021). However, Sutter et al. (2017) inferred nitrate from the SAM instrument on Mars, suggesting NO peaks at various temperatures from different nitrate samples. Navarro-González et al. (2018) found nitrite and nitrate labile in the presence of iron perchlorates, decomposing below 270°C, while magnesium and calcium chlorates or perchlorates cause nitrite to decompose below 400°C and nitrate above 400°C. Sutter et al.'s (2017) EGA results show NO peaks below 400°C in Cumberland, John Klein, and Rocknest samples, and above 400°C in other samples. Future work should investigate the thermal decomposition and photolysis of nitrite- and nitrate-bearing species in Mars-like soils to better interpret nitrite presence and understand the surface destruction of these species in different climates.

Data Availability Statement

KINETICS output files and Python analysis scripts are available at the open-source repository: (Adams, 2023).

Acknowledgments

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