# Nitrogen Fixation at Paleo-Mars in Icy Climates

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April 19, 2024

#### Abstract

Recent findings by the Mars Science Laboratory (MSL) have confirmed the presence of nitrates near Gale Crater on Mars. In this work, we consider the formation and deposition of HNOx species in cold early Mars climates. We find that solar energetic particles could facilitate nitrogen fixation by photochemically generating pernitric and nitric acid, which then deposit onto icy particles that settle onto Mars' surface. This study demonstrates that such deposition would be more efficient under higher atmospheric pressures, consistent with Mars' ancient atmosphere, and could account for the nitrate levels detected by the MSL. We find a more rapid deposition rate for pernitric acid over nitric acid (in agreement with Smith et al., 2014), and a significant enhancement of deposition rates through consideration of deposition onto icy particles. This distinction could be crucial for interpreting the MSL data.

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## 13 Abstract

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- 23 particles. This distinction could be crucial for interpreting the MSL data.
- 24

# 25 Plain Language Summary

- The MSL rover has detected NO from in surface soils, which is thought to come from nitrate in the soil. In this work, we make new estimates for deposition of pernitric acid in icy climates, and
- we discuss implications for interpreting the MSL measurements.
- 30 **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
- 33 330-1100 ppm of nitrate in the Klein and Cumberland Noachian-aged mudstone deposits,
- respectively, at Yellowknife Bay (Stern et al., 2015). Subsequent measurements of 0.002 to 0.05
- 35 wt% of nitrate in sediments near Gale Crater were also reported (Sutter et al., 2017). The
- 36 presence of nitrate suggests a nitrogen cycle during Mars' history. This would be relevant to
- 37 astrobiology, as nitrogen fixation is required for nitrogen to be useful to terrestrial life (e.g.,
- 38 Holm & Neubeck, 2009; Mancinelli & McKay, 1988). However, the precise mechanism of the
- 39 nitrogen cycle on early Mars remains debated.
- 40 Adams et al. (2021) recently described how these nitrates could have been formed by
- 41 lightning-induced nitrogen fixation in a warm and wet climate. The assumed warm climate was
- 42 motivated by significant geochemical and geomorphological evidence that suggests warm wet
- 43 climate episodes of  $10^5$ - $10^7$  years duration (e.g., Carr et al., 2003; Clifford et al., 2001; Barnhart
- 44 et al., 2009; Hoke et al., 2011; Olsen et al., 2007). However, the globally averaged surface
- 45 deposits of nitrate predicted by Adams et al. (2021) are consistent only with the lower limits of
- the MSL measurements, and the climate would have likely only been warm and wet for a brief

47 window of Mars' history (e.g., Wordsworth et al., 2016). Since cold, icy climates likely persisted

for longer during Mars' total history, it remains interesting to examine whether nitrates couldhave formed during the cool periods too.

- 50 Mancinelli (1996) predicted the formation of nitrates at early Mars would arise via the
- following chemical pathways: First, photodissociation of  $N_2$  and ion-neutral reactions are known to form odd nitrogen radicals in the thermosphere, and upon transporting downwards, these
- 52 species may then be oxidized to form nitric acid (e.g., Krasnopolsky, 1993; Yung et al., 1977).
- 54 Smith et al. (2014) also considered formation and dry deposition of nitric and pernitric acid in 7
- 55 and 35 mbar Amazonian atmospheres. They found dry deposition of the latter exceeded the
- 56 former by two orders of magnitude and N accumulation during the Amazonian of 0.4-0.2 wt% if
- 57 mixed uniformly to a depth of 1.5-2.6 m. In this work, we seek to improve estimates by
- 58 considering: five climate scenarios with surface pressures ranging from 7 mbar 1 bar
- 59 (representative of Mars' climate change through time from Noachian to Amazonian); adding
- 60 energy deposition from solar energetic particles; and adding adsorption of HNOx species onto
- 61 atmospheric ice particles which settle onto Mars' surface.
- 62

# 63 **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 including

- 57 Jupiter (e.g., Moses et al., 2005), Titan (e.g., Li et al., 2014), and Pluto (see, e.g., Wong et al.,
- 68 2015), and a similar approach was considered for nitrogen fixation in warmer climates for the 69 early Earth in Wong et. al. (2017) and for early Mars in Adams et al. (2021).
- The model solves the 1D continuity equation by computing the chemical production and loss rates at each layer, as well as the diffusive flux between each layer:
- 72

$$\frac{n_i}{lt} = P_i - L_i - \frac{\partial \phi_i}{\partial z},\tag{1}$$

where  $n_i$  is the number density of species *i*,  $P_i$  the chemical production rate,  $L_i$  the chemical loss rate, and  $\phi_i$  the vertical flux, all considered at time *t* and altitude *z*. The vertical flux is given by

75

$$\phi_i = -D_i \left( \frac{\partial n_i}{\partial z} + \frac{n_i}{H_i} + \frac{1 - \alpha_i}{T} \frac{\partial T}{\partial z} n \right) - K_{ZZ} \left( \frac{\partial n_i}{\partial z} + \frac{n_i}{H_a} + \frac{1}{T} \frac{\partial T}{\partial z} n \right), \tag{2}$$

- where  $D_i$  is the species' molecular diffusion coefficient,  $H_i$  the species' scale height,  $\alpha_i$  the thermal diffusion parameter,  $H_a$  the atmospheric scale height, *T* the temperature, and  $K_{zz}$  the vertical eddy diffusion coefficient, (Yung & DeMore, 1999). The flux consists of molecular diffusion (which is derived from the molecular theory of ideal gases) and eddy transport. We
- calculate the eddy diffusion coefficient profile according to the formulation in Ackerman and
  Marley (2001). The two terms largely differ according to the scale height: eddy diffusion follows
- the bulk atmospheric scale height  $(H_a)$  which leads to a well-mixed atmosphere, but molecular
- diffusion drives each species to follow its own scale height ( $H_i$ ) which drives the system toward
- 84 diffusive equilibrium in the case of an isotherm.
- 85 We investigate icy nitrate formation in five cold climates: 7 mbar, 50 mbar, 200 mbar,
- 500 mbar, and 1 bar, and we consider the chemistry of the following species linked by 152
- 87 reactions on an altitude grid with 1-2 km spacing up to 118 km: O, O(1D), O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, H, H<sub>2</sub>,
- 88 OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, N, N(2D), NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>5</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, HO<sub>2</sub>NO<sub>2</sub>, CO, O<sup>+</sup>, O<sub>2</sub><sup>+</sup>,

 $CO_2^+$ ,  $CO_2H^+$ , and electrons. The full reaction list and the column rates are provided in Table S1. 89 We fix the mixing ratios of N<sub>2</sub> and CO<sub>2</sub> to 2.7 and 97.3% according to the annual mean of 90 present day measurements, ignoring the presence of Ar (Trainer et al., 2019) and to 10 and 90% 91 92 in the thicker atmospheric cases motivated by previous works that suggest larger N<sub>2</sub> abundances 93 in the past (e.g., Hu & Thomas, 2022). We fix the concentration of H<sub>2</sub>O to the saturation vapor 94 pressure in the lower atmosphere and assume it becomes cold trapped to a steady mixing ratio in 95 the stratosphere. We adopt the temperature-pressure profiles computed by Adams et al., in review, which used a 1D radiative-convective model to compute the TP profiles expected by the 96 97 steady state chemistry in each case. We consider their CO<sub>2</sub> dominated atmospheres with low H<sub>2</sub> 98 content, and these TP profiles look similar to profiles in previous radiative-convective simulations (e.g., Kasting, 1991; Wordsworth et al., 2017). Unless otherwise stated, we set the 99 flux at the upper and lower boundaries for each species to be zero. At the lower boundary, we fix 100 101 the concentration of water vapor to the concentration equivalent to the saturation vapor pressure 102 and the concentration of all ion species to zero. We consider a deposition velocity of nitrous, nitric, and pernitric acid of 0.02 cm s<sup>-1</sup> (Krasnopolsky 1993; Smith 2014), and a small deposition 103 velocity for  $O_2$ ,  $O_3$ , and CO of  $10^{-6}$  cm<sup>-2</sup>s<sup>-1</sup>. We consider a flux of N and N<sup>(2D)</sup> into the 104 atmosphere at the upper boundary to represent deposition of solar energetic particles, and which 105 we estimate from the Geant4 simulation results in Adams et al. (2021). In the 7-mbar case we 106 107 set the mixing ratios of O<sub>2</sub>, H<sub>2</sub>, and CO at the lower boundary according to present day measurements. At the upper boundary, we fix the escape flux of O to  $1.2 \times 10^8$  molecules cm<sup>-2</sup> s<sup>-1</sup> 108 (Nair et al., 1994), which is in agreement with present-day observations (e.g., Jakosky et al., 109 110 2018; references therein), and we fix the escape velocity of H and H<sub>2</sub> to  $3.08 \times 10^3$  and  $3.39 \times 10^1$ 111 cm s<sup>-1</sup>, respectively, according to diffusion-limited escape theory (e.g., Hunten et al., 1972). We 112 consider that the solar spectrum will have changed over time, assigning an earlier flux (3.8 Ga) 113 for the 500 and 1000 -mbar cases, intermediate-age (2.7 Ga) for the 50 and 200 mbar cases, and 114 a present-day flux for the 7-mbar case. We parametrize these changes according to Claire et al. 115 (2012). We fix the ice particle distribution, and we assume all HNOx deposited onto ice is 116 eventually lost.

Water ice amounts are based on profile retrievals of water ice extinction from measurements by the Mars Climate Sounder (MCS) (Kleinböhl et al. 2009, 2017). We average MCS observations for Mars years 29-33 for the 5 Ls periods 0-5, 45-50, 90-95, 135-140, and 175-180 and compute number densities and cross-sections of ice particles based on the particle size distribution from Kleinböhl et al. (2011) with an effective particle radius of 1.41 microns. We prescribe a rate coefficient for loss of a species through heterogeneous reactions with ice aerosols as:

$$J' = \frac{1}{4} \gamma \nu \sigma N_{ice}$$
(3)

124 where  $\gamma$  describes the sticking coefficient,  $\nu$  describes the thermal velocity of the gas,  $\sigma$ 

125 describes the average cross section (area) of the ice particle, and  $N_{ice}$  describes the number

126 density of the ice particles (e.g., Yung & DeMore 1982). We consider a  $\gamma$  of 0.01 according to

127 Michelangeli et al. (1989). The computed time-averaged J' profile is plotted in black in Figure

- 128 S1, and the temporal variations are overlaid behind in various colors. The earlier atmospheres
- 129 would have likely hosted greater ice concentrations due to the higher pressures; due to the
- 130 uncertainty, we scale the present-day ice concentrations by a factor f which we vary over 1x, 3x,
- 131 and 10x for all climate scenarios considered.
- 132

### 133 3. Results: Photochemical Production of Nitric and Nitrous Acid

- The destruction of  $N_2$  is driven by solar energetic particles (SEPs) in the upper atmosphere, and the products are oxidized to produce NO. NO may directly produce HNO<sub>2</sub> through reacting with OH, or it may produce the other NOx species through reactions with O and HO<sub>2</sub>. Some NO may also react with N to form N<sub>2</sub>O, and which often cycles the fixed-N back to N<sub>2</sub> through photolysis and reactions with O(<sup>1</sup>D). N<sub>2</sub>O reacting with O(<sup>1</sup>D) may also form 2 NO. NO<sub>2</sub> contributes to formation of both nitrous acid (HNO<sub>2</sub>) and pernitric acid (HO<sub>2</sub>NO<sub>2</sub>) through
- 140 reactions with HO<sub>2</sub>, and in a self-terminating reaction the NOx species NO<sub>2</sub> and NO<sub>3</sub> form  $N_2O_5$ .
- 141 While  $NO_3$  and  $N_2O_5$  are both generally susceptible to destruction by photolysis, this  $N_2O_5$  may
- also react with water vapor or heterogeneously with water ice to produce nitric acid (HNO<sub>3</sub>). The
- 143  $HNO_x$  species may then be absorbed onto ice particles and deposited to the surface. These
- 144 chemical pathways are summarized in Figure 1.



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Figure 1. Cartoon of the relevant odd-nitrogen chemistry in Mars' atmosphere. N<sub>2</sub> dissociation
 by SEPs causes NO formation, oxidation of which leads to HNOx production and deposition.

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149 The steady state mixing ratios which result from this chemistry are shown in Figure 2. 150 The energy deposited and thereby the rate of N<sub>2</sub> destruction is the same in all climate scenarios, 151 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 152 153 higher altitudes only. For similar reasons, 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 154 NO decreases slower than that of N due to both a greater availability of HOx in the thicker 155 156 atmospheric cases, since its production rate scales with the concentrations of both N and the oxidant, as well as the additional source of NO from N<sub>2</sub>O photolysis. For similar reasons, the 157 mixing ratios of HNOx are relatively more consistent across the different atmospheric densities. 158

159 For example, in the case of the lowest ice concentration (solid pink lines), the near-surface  $HO_2NO_2$  is near ~10<sup>-12</sup> (within a factor of ~3) for all atmospheric pressures. However, in the 160 cases with more ice in the 200 mbar atmosphere, the limited availability of lower atmosphere N 161 162 and NO causes much smaller near-surface mixing ratios of HNOx species. The ice content not only removes HNOx faster but also H<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub>, which influences the redox state of the 163 164 atmosphere and slows the reactions which oxidize N and NO. Additionally, in thinner 165 atmospheric cases, the lower density and constant destruction rate of  $N_2$  makes NO more likely 166 to collide and react with N, which forms N<sub>2</sub>O and ultimately recycles the NOy species back to 167 N<sub>2</sub>. Therefore, in thicker atmospheric cases, a greater fraction of the produced NO will go on to 168 form nitrous and nitric acid. The formation of nitric acid requires reactions with water vapor, and 169 the thicker atmospheric cases foster greater saturation vapor pressures of water. (The water vapor 170 also extends to higher altitudes in the cases of higher pressure, but this is less significant since 171 the N- and NOx- availability also become more limited to higher altitudes in these cases due to 172 more frequent collisions.) Therefore, the steady state mixing ratios of nitric acid are greater in

- 173 the 500-mbar case than the 50- and 200-mbar cases.
- 174 The cases with greater ice abundances result in faster loss of HNOx and  $N_2O_5$ , partially 175 due to the adsorption onto the particles and heterogeneous reactions, respectively. The larger ice
- abundance also causes faster removal of  $H_2O_2$ , causing a decrease in OH and atmospheric
- 177 oxidants. This causes a small increase in N and contributes to slower production of NO and
- 178 HNOx species, which are largely produced through reactions with HOx.



181 Figure 2. Mixing ratios of nitrous acid (blue), nitric acid (orange), pernitric acid (magenta), and



183 (magenta), and N<sub>2</sub>O (grey) are shown in the lower panels. Five climate scenarios are considered

184 from left to right: 7 mbar, 50 mbar, 200 mbar, 500 mbar, and 1 bar. In each panel, the ice

concentration is varied from 1x (solid), 3x (dashed), and 10x (dotted linestyle) the temporal
average from MCS data as described in Figure S1.

187

## 188 4. Results: Deposition Rate of HNOx on Ice Particles

189 We find that deposition of HO<sub>2</sub>NO<sub>2</sub> generally dominates the flux of HNO<sub>x</sub> species to Mars' surface in icy climates, as summarized in Figure 3. This differs from terrestrial chemistry, 190 191 where nitric acid deposition is faster than that of pernitric acid because of rapid thermal 192 decomposition in the lower troposphere; however, this rate has a strong temperature dependence 193 and is orders of magnitude slower from tens of degrees of cooling (Graham et al., 1978; Gierczak 194 et al., 2005). The rate of thermal decomposition of HO<sub>2</sub>NO<sub>2</sub> in the cool 1-bar early Mars 195 atmosphere is slower than photolysis at the surface by more than 2 orders of magnitude at 200 K 196 and by ~4 orders of magnitude at 180 K. This HO<sub>2</sub>NO<sub>2</sub> is formed fastest in the thicker 197 atmosphere cases due to a pressure dependence of the rate for its main production pathway: HO<sub>2</sub> 198  $+ NO_2 + M \rightarrow HO_2NO_2 + M$ . On the other hand, the formation of nitric acid at early Mars 199 occurs through several reactions, all of which are slower than pernitric acid production: In the 200 thicker atmospheres, N<sub>2</sub>O<sub>5</sub> may react with water to form nitric acid, but this is primarily limited 201 to the lowest  $\sim 20$  km, where water vapor concentrations are largest. In the thin atmospheres, both water vapor and N<sub>2</sub>O<sub>5</sub> abundances are low and instead, production of HNO<sub>3</sub> near the surface 202 203 requires that NO<sub>3</sub> become oxidized by HO<sub>2</sub>; however, the NO<sub>3</sub> concentrations are smaller than 204 NO<sub>2</sub> by several orders of magnitudes (thereby again favoring pernitric acid over nitric acid 205 formation). In all cases, nitric acid production in the upper atmosphere (which is relatively dry) 206 is limited to oxidation of NO<sub>2</sub> by OH, but like other HNOx species, the near-surface production 207 (by the previously mentioned reactions) is faster.

208 209





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

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The deposition rates of both pernitric 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. HO<sub>2</sub>NO<sub>2</sub> is primarily formed when HO<sub>2</sub> attacks NO<sub>2</sub>, and this
- reaction occurs  $\sim 10x$  faster in the 500 mbar case than in the 50 mbar case (see Figure 4)
- primarily due to a pressure dependence of the 3-body reaction:  $HO_2 + NO_2 + M$ . The
- 223 concentration of  $NO_2$  also influences this rate.  $NO_2$  is larger in the thicker atmospheres (500 224 mbar and 1 bar) due to greater amounts of  $O_3$  available to oxidize NO to  $NO_2$  compared to the
- thinner cases (7 and 50 mbar). However, the 200-mbar case sees a depletion in  $NO_2$  due to a
- 226 limited availability of HOx in the upper atmosphere, which limits conversion from N to NO.
- 227 This may be due to a larger CO abundance, where the greater  $CO_2$  photolysis rate depletes the
- 228 upper atmosphere of oxidants in order to convert CO back to CO<sub>2</sub>. The production of nitric acid
- is faster in the thicker atmospheres largely due to the reaction  $N_2O_5 + H_2O$  becoming the
- dominant pathway (see Figure 4). This is attributed to a greater availability of surface liquid
- 231 water (directly caused by the greater pressures) and of  $N_2O_5$ . The near-surface  $N_2O_5$
- 232 concentration increases with surface pressure with a notable transition occurring between the
- 233 200-mbar and 500-mbar cases. The greater  $NO_2$  concentrations facilitate faster formation of
- 234 NO<sub>3</sub>, both of which increase the rate of N<sub>2</sub>O<sub>5</sub> production.
- 235



### 236

**Figure 4.** Reaction rates (cm<sup>-3</sup>s<sup>-1</sup>) for loss by photolysis (upper panel) and production (lower panel) reactions for HNOx species. Different climate scenarios are shown in panels from left to right: 7 mbar, 50 mbar, 200 mbar, 500 mbar, and 1 bar. For clarity within each panel, only the 1x J<sub>ice</sub> case is shown.

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With several assumptions, we can approximate to an order of magnitude the concentration of salts that have accumulated in the Mars soil. We attempt to roughly estimate

- the duration of each of our four surface pressures by discretizing the rate of atmospheric  $CO_2$
- loss described in Hu et al. (2015) and extrapolating back to 4.1 Gya (the start of the Noachian);
- although we acknowledge these are highly uncertain and that the surface pressure would have
- 247 likely decreased more smoothly over time: ~300 Myr each in the 1-bar, 500-mbar, 200-mbar,

248 and 50-mbar climates and the remainder of Mars' history (~3 Gyr) in the 7-mbar climate. From 249 this, we find that most nitrite and nitrate deposition occurs during the 1-bar and 500-mbar 250 climates. Following deposition on ice and settling of the ice to the surface, we assume the soils 251 are mixed throughout a shallow depth due to post-Noachian impactors. We consider ~2m which represents three e-folding depths (Zent 1998). We also assume a soil density of 1 g/cc (Moore 252 253 and Jakosky, 1989). These assumptions are consistent with those in Smith et al. (2014). We 254 assume the loss rates of nitrate and nitrite following deposition would be negligible. Nitrates in 255 ice cores are thought to be long-lived and have been used as proxies at Earth for studying the 256 occurrence of past SEP events (Dreschhoff & Zeller, 1990; Schrijver et al., 2012). We assume no 257 aqueous systems existed during this part of Mars' history, although short aqueous episodes could 258 have invoked new loss mechanisms including photoreduction, loss to iron, and hydrolysis 259 (Ranjan et al., 2019; Wong et al., 2017). In this scenario, loss to photoreduction would be particularly fast ( $\tau \sim 1$  year; Mack and Bolton, 1999). Under these assumptions, our 1x ice case's 260 deposition fluxes correspond to the following weight percents: ~4 wt% NO from nitrate, ~8 wt% 261 NO from nitrite. This is much greater than the MSL findings (70-1100 ppm; Sutter et al., 2017; 262 263 Stern et al., 2015), suggesting that nitrate and nitrite were likely altered on Mars' surface and lost 264 over time. This paper only seeks to describe the atmospheric formation of nitrate in the 265 atmosphere and delivery to the surface, so we encourage future works to investigate surface loss 266 processes for surface nitrate in cold climates (such as cosmic rays) or to better constrain the 267 occurrence and duration of short aqueous episodes at Mars through time.

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### 269 5. Discussion: Interpreting the Formation of MSL-Measured Volatiles

We find that icy climates are able to form and deposit nitric acid fast enough to produce global-average nitrate deposits at least as large as the MSL-measurements, although we acknowledge that the MSL measurements may not be globally representative (e.g., ices and/or NOx could transport to locally collect in some regions).

274 Our result does not rule out the formation of nitrates in warm and wet climates (e.g., 275 Adams et al., 2021). However, it suggests the nitrates measured by MSL could be formed by two 276 mechanisms at different epochs in time. Future measurements of N-isotopes in the Martian 277 nitrates could help constrain when the nitrates formed. Over Mars' history, the atmospheric 278 isotopic record became enriched in heavy isotopes due to atmospheric loss to space; since nitrate 279 formation originates with atmospheric chemistry under both regimes, nitrates formed during the 280 warm and wet climate would likely be older and thus of lighter isotopic signatures than nitrates 281 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  ${}^{14}N/{}^{15}N$ . 282

283 Our results demonstrate that the deposition of pernitric acid may have been faster than 284 that of nitric acid, in agreement with Smith et al. (2014). Importantly, there appears to be a 285 surface pressure dependence for the total rain out rates of HNOx species and the relative rain out 286 rates of pernitric vs nitric acid. The fate of pernitric acid upon deposition may be analogous to its 287 fate in aqueous systems, in which its destruction would result in nitrite salts on the surface (e.g., 288 Regimbal and Mozurkewich, 1997; Slusher et al., 2002). However, Sutter et al. (2017) reports 289 only detections of nitrate at Mars from the SAM instrument, inferred from multiple NO releases 290 from soil samples in the evolved gas analysis (EGA) experiment; they suggest NO peaks at 291 various temperatures may result from NO evolved from different samples including Fe-bearing

292 nitrates, which evolve at relatively lower temperatures, and Mg-, Ca-, Na- and K-bearing

293 294 295 296 297 298 299 300 301 302 303 304	nitrates, which evolve at relatively higher temperatures (e.g., Gordon and Campbell, 1955; Mu and Perlmutter, 1982; Ettarh and Galwey, 1996; Stern et al., 2015). It may be interesting to question whether the evolved NO could suggest the presence of nitrite. Navarro-González et al. (2018) discovered that both nitrite and nitrate are extremely labile in the presence of iron perchlorates decomposing at temperatures below 270 C; however, in the presence of magnesium and calcium chlorates or perchlorates, NO2 <sup>-</sup> decomposes below 400 C and nitrate decomposes above 400 C. The EGA results of Sutter et al. (2017) show NO peaks at temperatures below 400 C in the Cumberland, John Klein, and Rocknest samples; NO peaks at temperatures greater than 400 C are in several other samples. We suggest that future work investigate the thermal decomposition of nitrite- and nitrate- bearing species in Mars-like soil samples in order to place better constraints on interpreting the presence or absence of nitrite.
305 306 307 308	<b>Open Research</b> KINETICS output files and Python analysis scripts are available at the open-source repository (Adams, 2023).
309 310 311 312 313	Acknowledgements We thank Dr. Glenn Orton and Dr. Steve Vance for helpful comments on the manuscript. Work at the Jet Propulsion Laboratory, California Institute of Technology, is performed under contract with the National Aeronautics and Space Administration (80NM0018D0004).
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Figure 1.



Figure 2.



Figure 3.



Figure 4.

