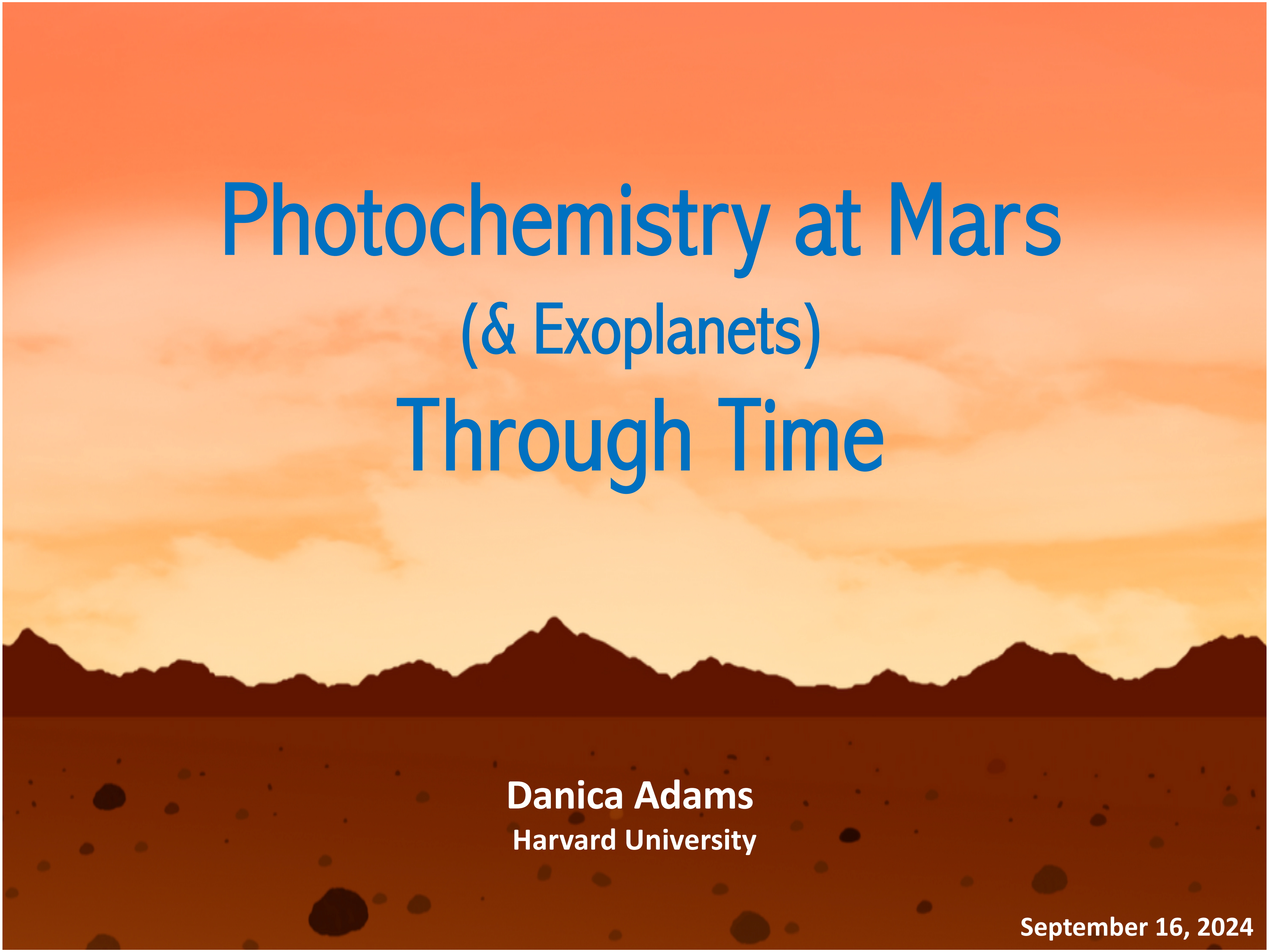
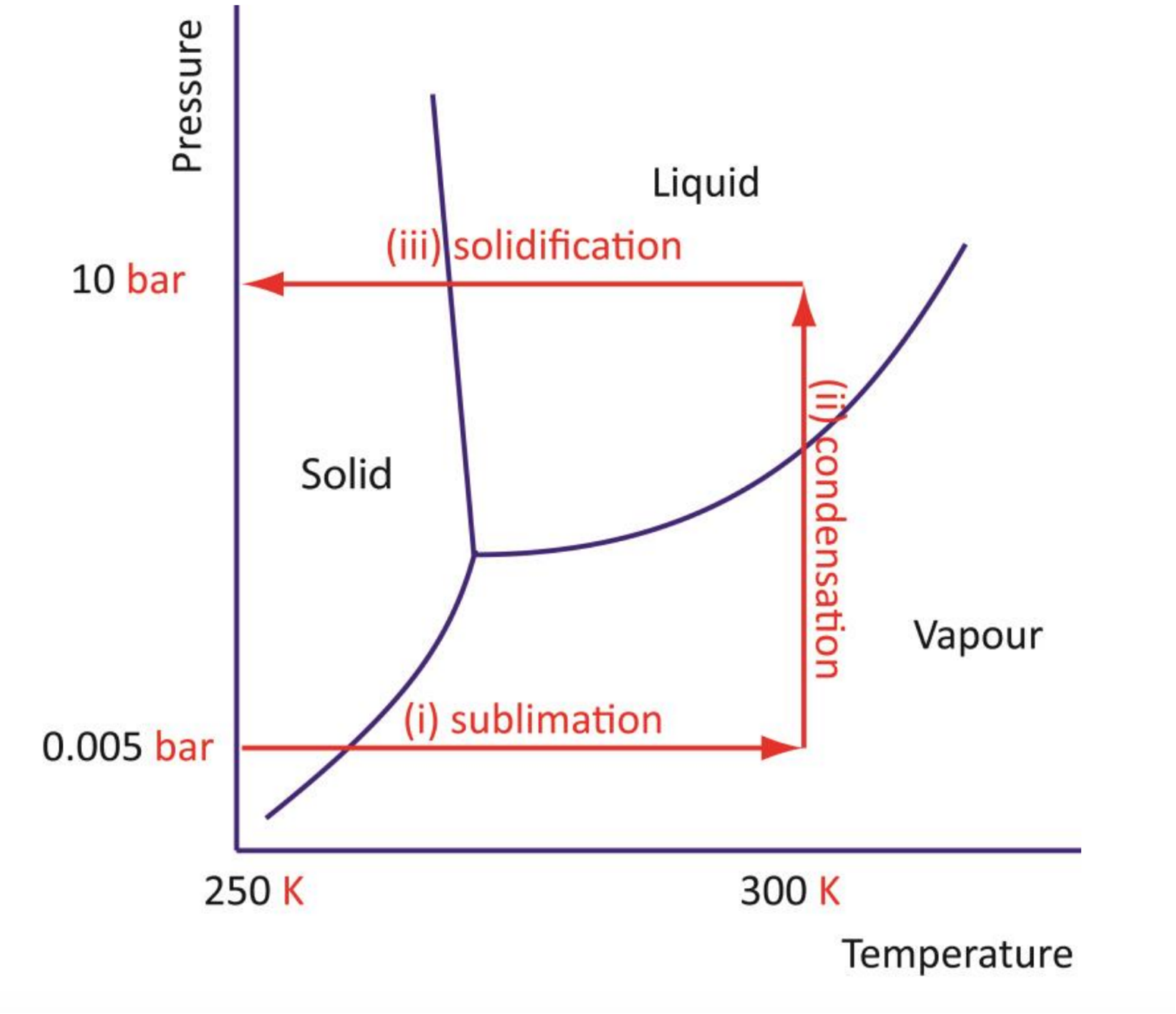


Photochemistry at Mars
(& Exoplanets)
Through Time

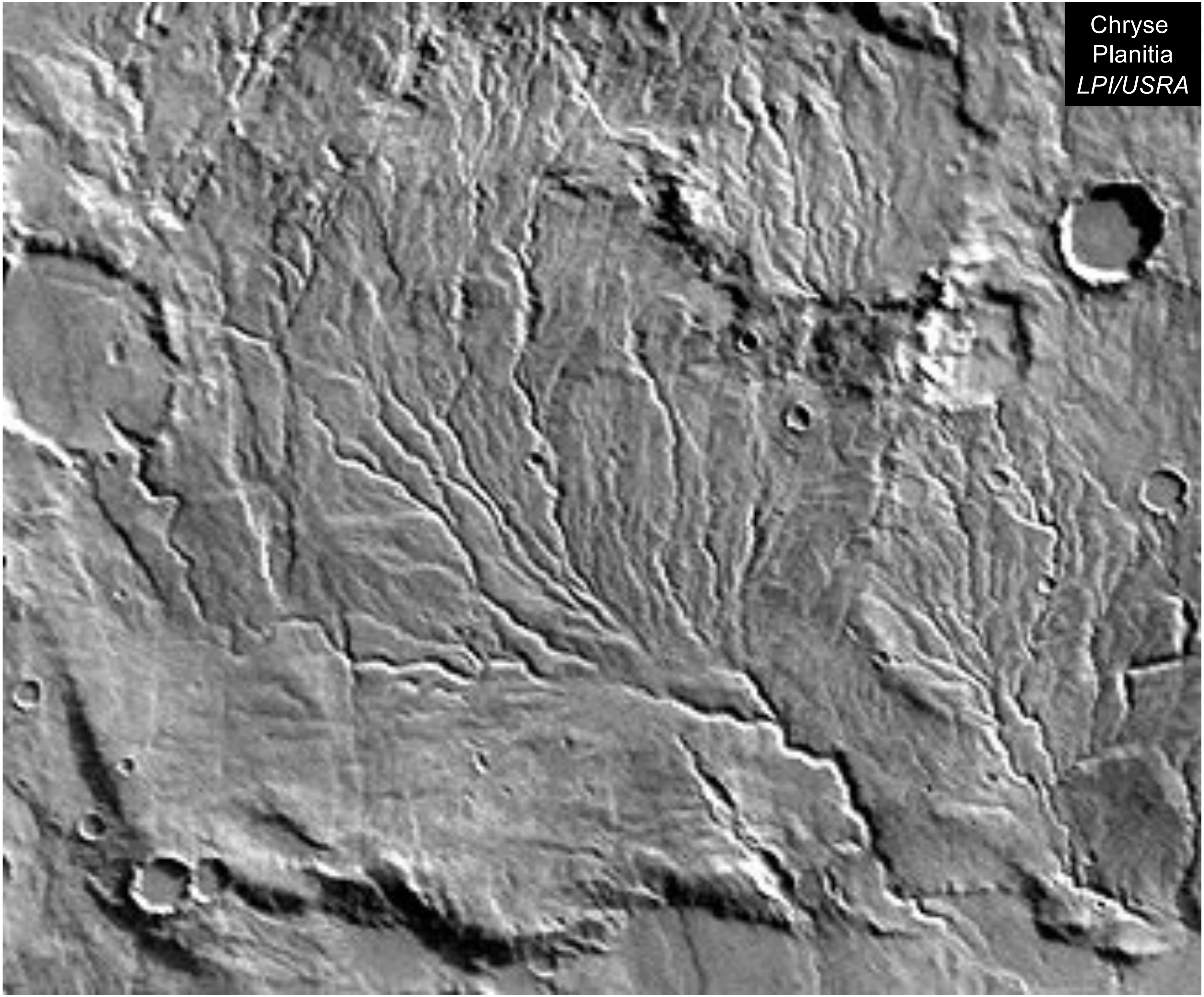
Danica Adams
Harvard University

September 16, 2024

Today, Mars' atmosphere is too cold and thin to sustain surface liquid water.



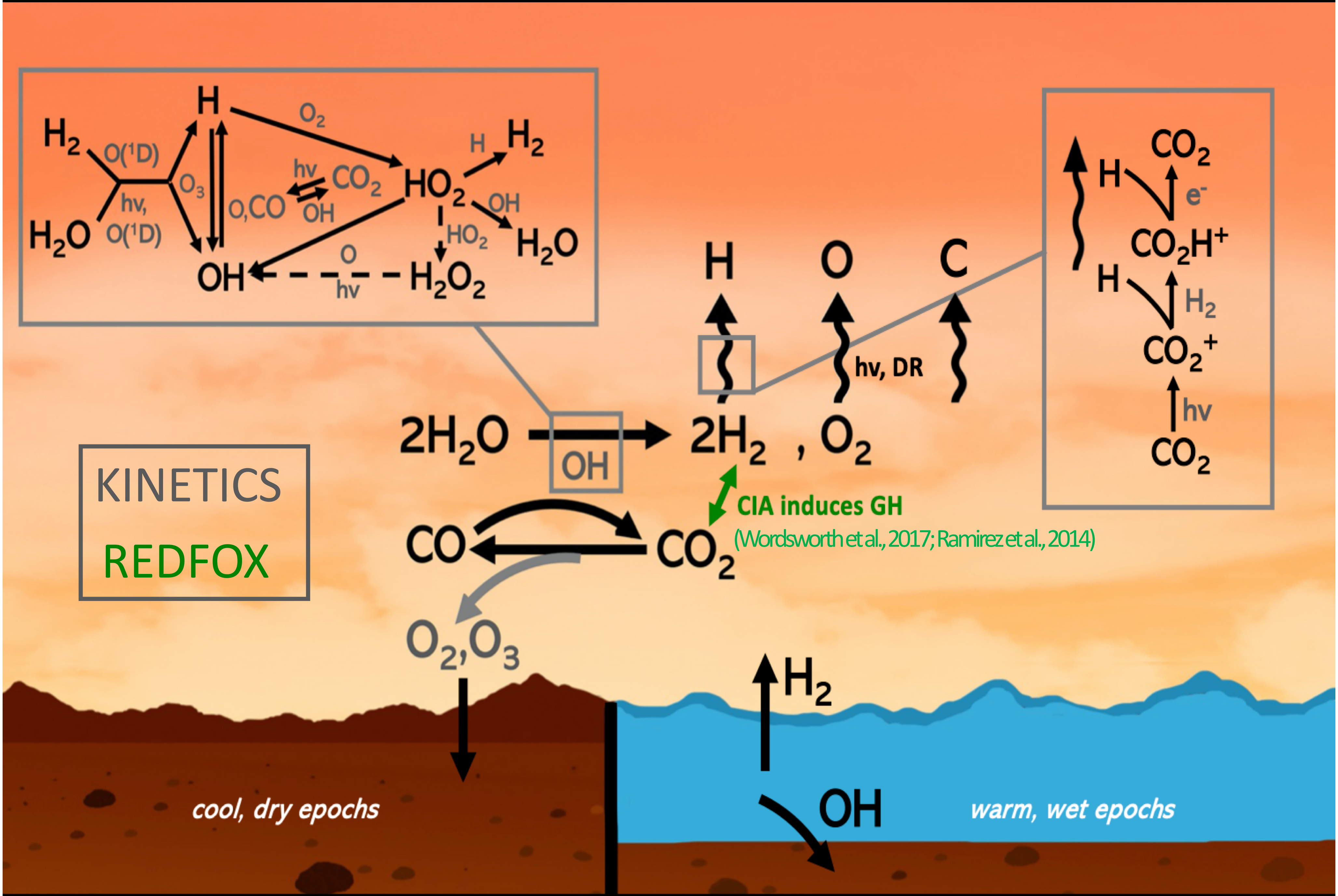
PC: Burrows, *Chemistry 3rd Ed.*



Chryse
Planitia
LPI/USRA

What could have warmed early Mars?

Mastcam onboard Curiosity



Adams et al., *in review Nature Geoscience*

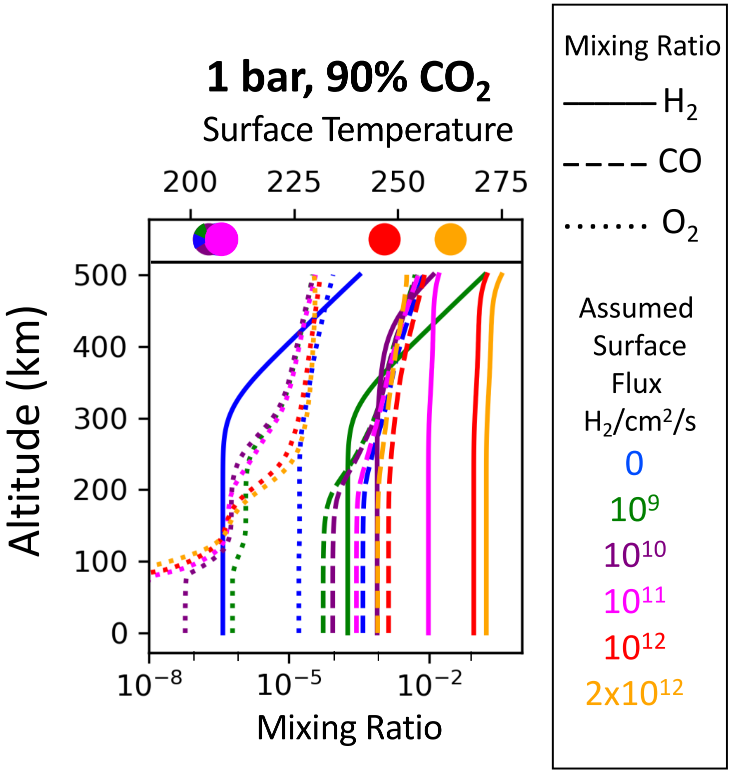
In Warm Climates:

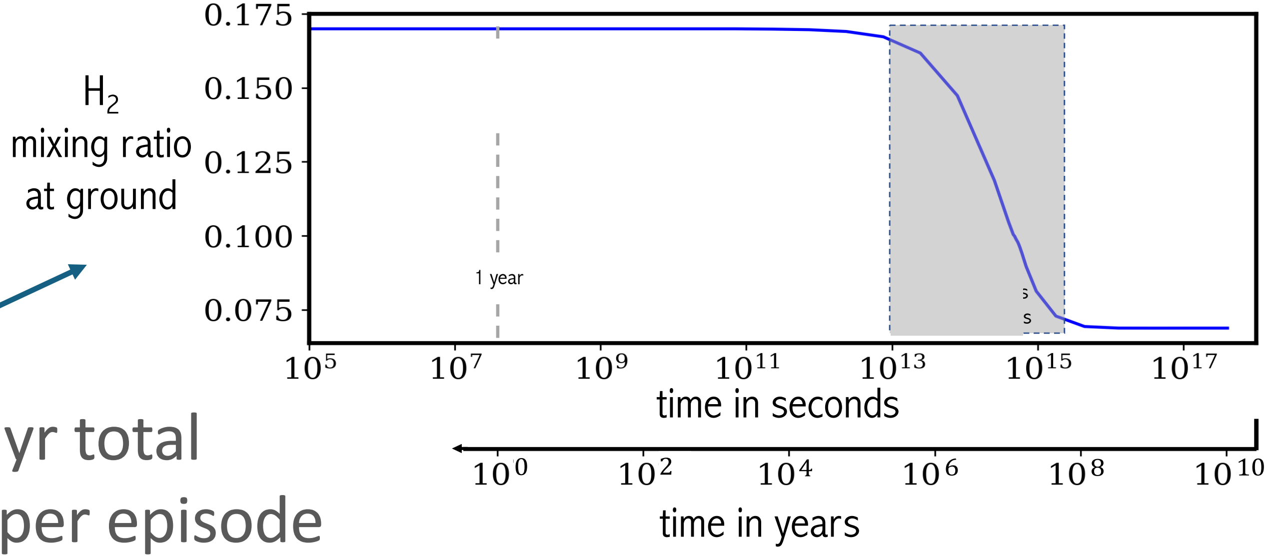
H_2 supplied by

- 4-400m GEL H_2O to crustal hydration
- 30-380m GEL H_2O to iron oxidation

$$2\,\mathrm{FeO} + \mathrm{H_2O} \longleftrightarrow \mathrm{Fe_2O_3} + \mathrm{H_2}$$

Ts > 250 K to support local surface liquid water



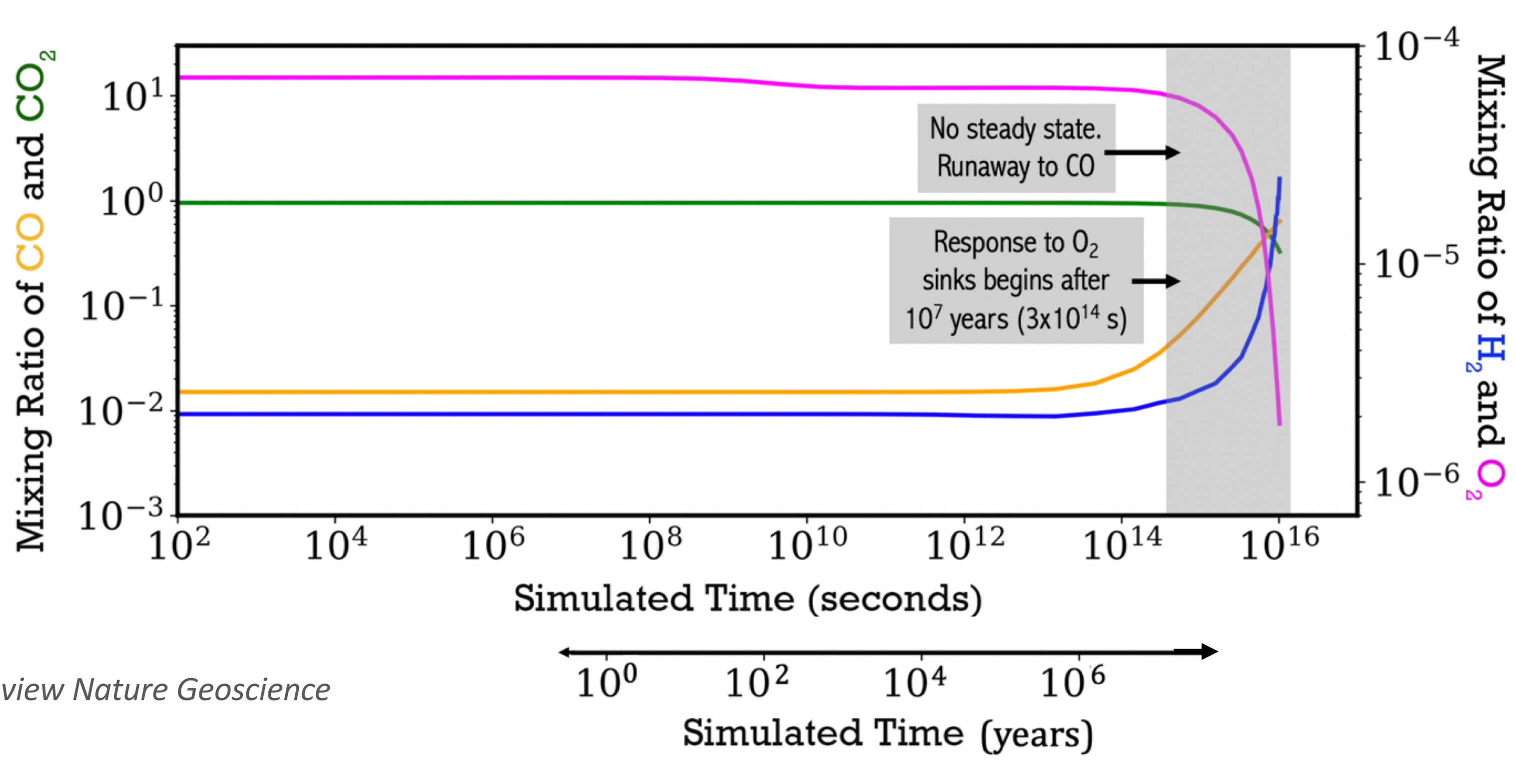


H_2-rich for up to 40 Myr total

H_2-rich for ≥ 0.1 Myr per episode

Adams et al., *in review Nature Geoscience*

In Cool Climates: $CO_2 + hv \rightarrow CO + O$, $CO + \underline{OH} \rightarrow CO_2 + H$



No steady state. Runaway to CO

Response to O_2 sinks begins after 10^7 years ($3x10^{14}$ s)

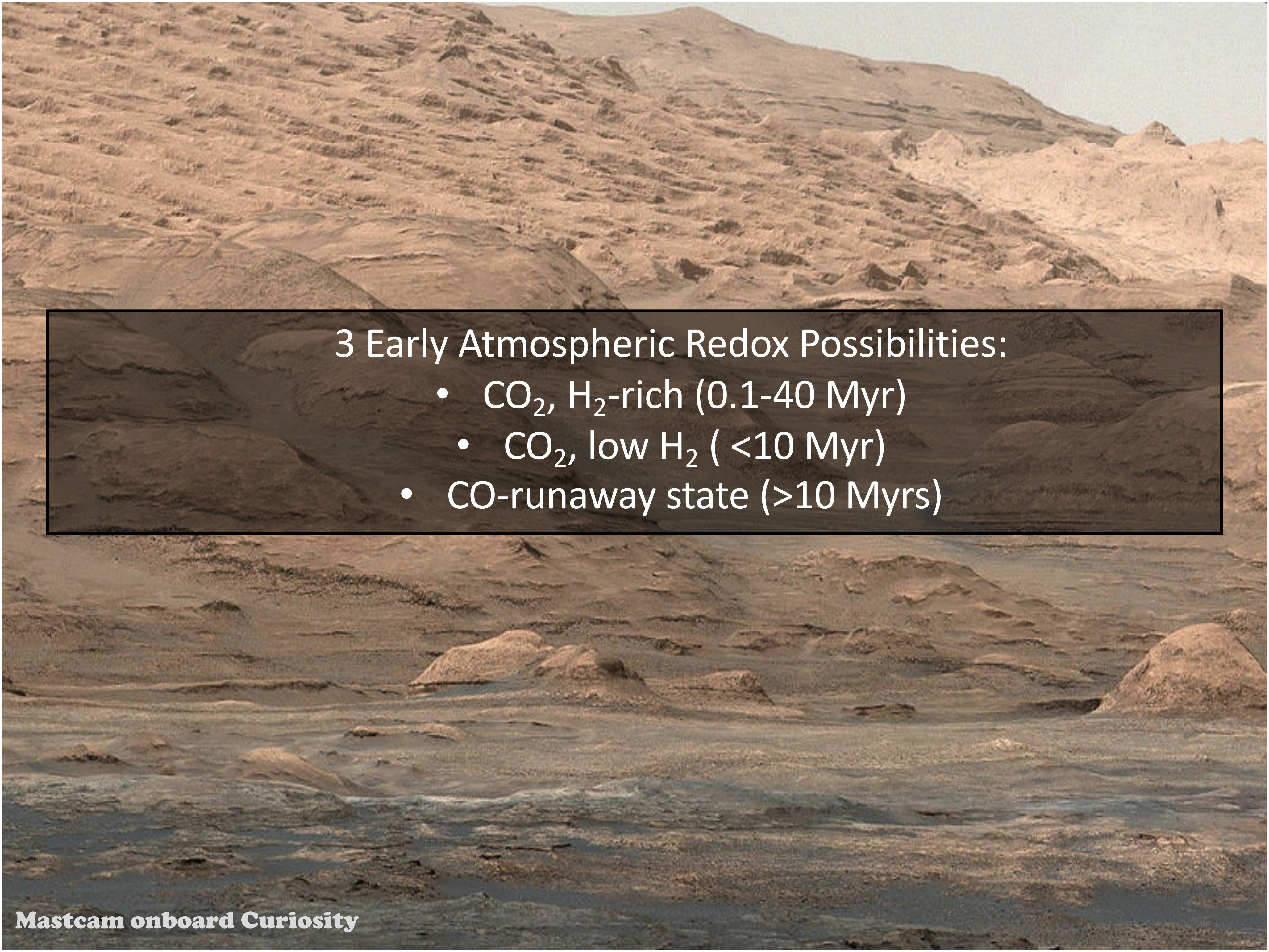
Adams et al., *in review Nature Geoscience*

Sensitivities in HOx chemistry may drive ~2x more CO runaway

Smith, Adams, et al., in prep for resubmission

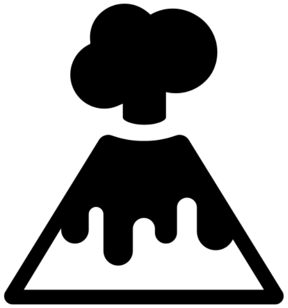
3 Early Atmospheric Redox Possibilities:

- CO_2, H_2-rich (0.1-40 Myr)
- CO_2, low H_2 (<10 Myr)
- CO-runaway state (>10 Myrs)

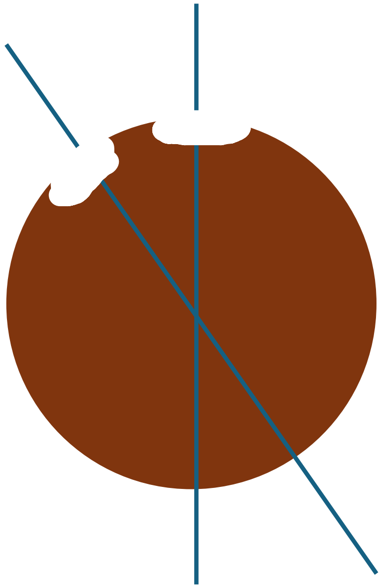


Mastcam onboard Curiosity

Cold-to-Warm

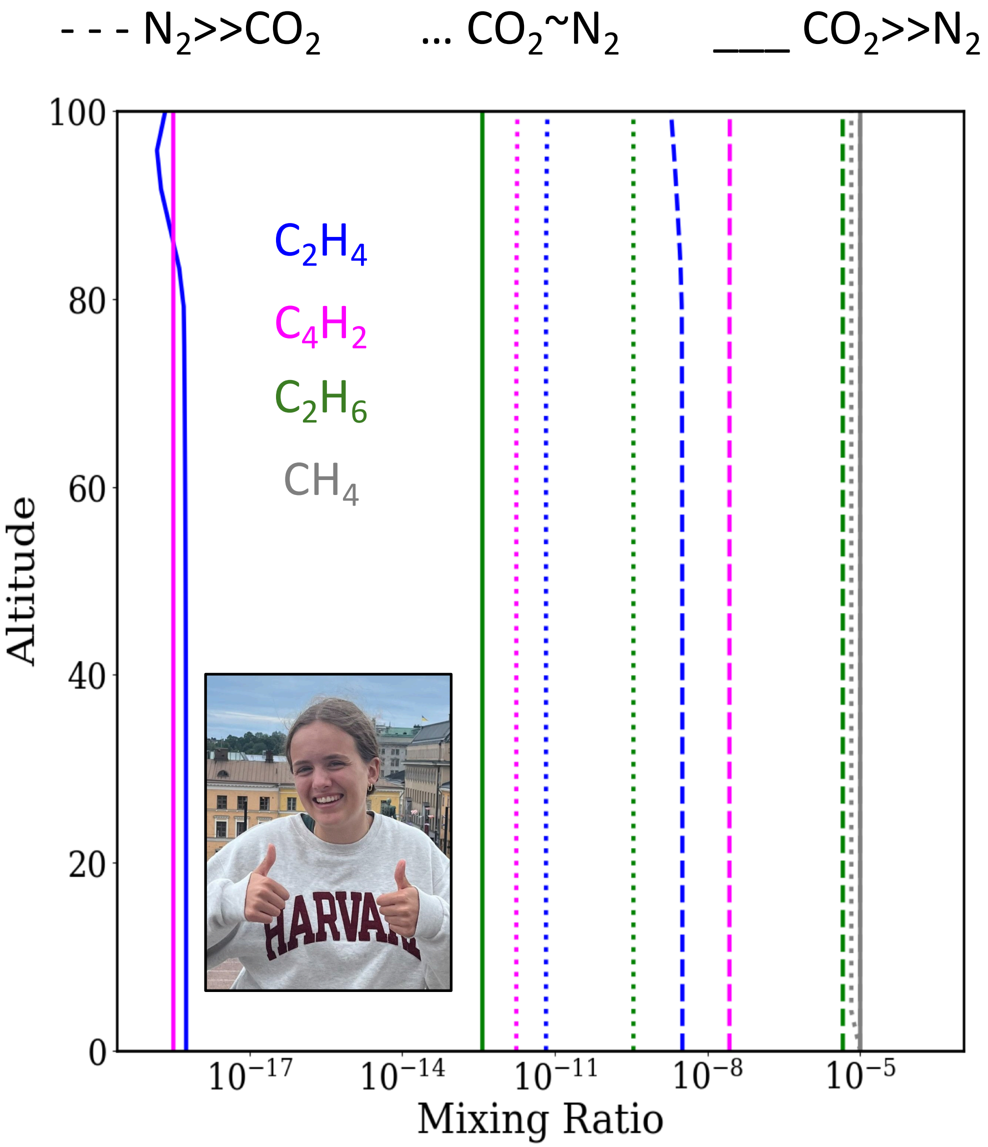


Ramirez et al. (2014)



CH_4: Kite et al. (2020)
H_2: Adams et al., in review

Hydrocarbons?

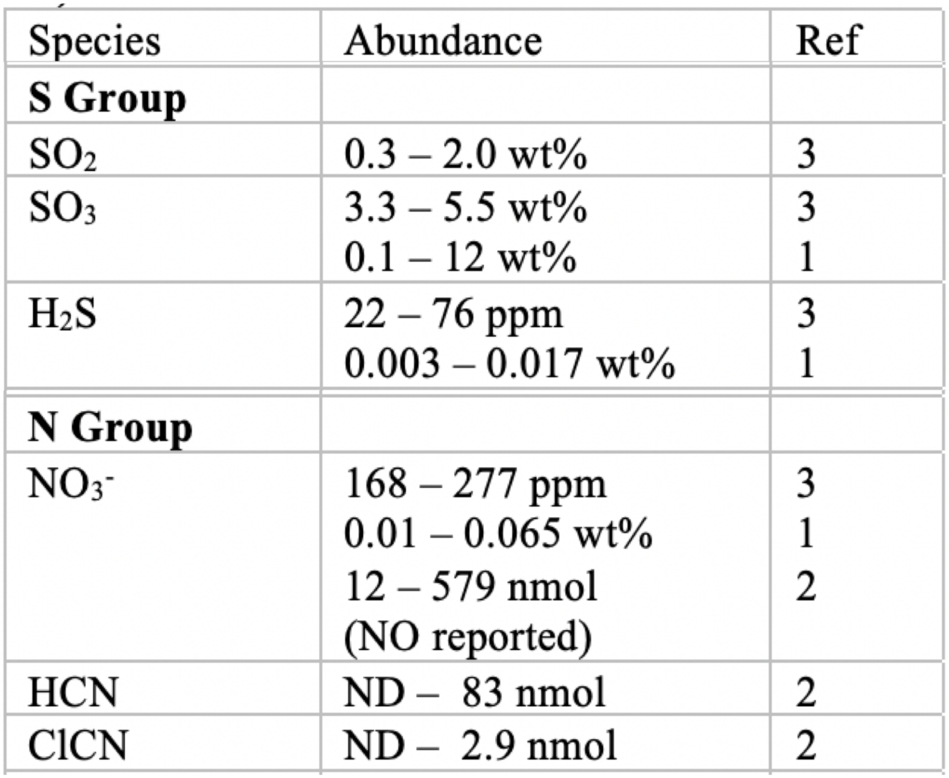


Thomas, Adams, et al., in prep

Evidence for Changing Redox Over Time?

The Importance of Mars Sample Return (MSR)

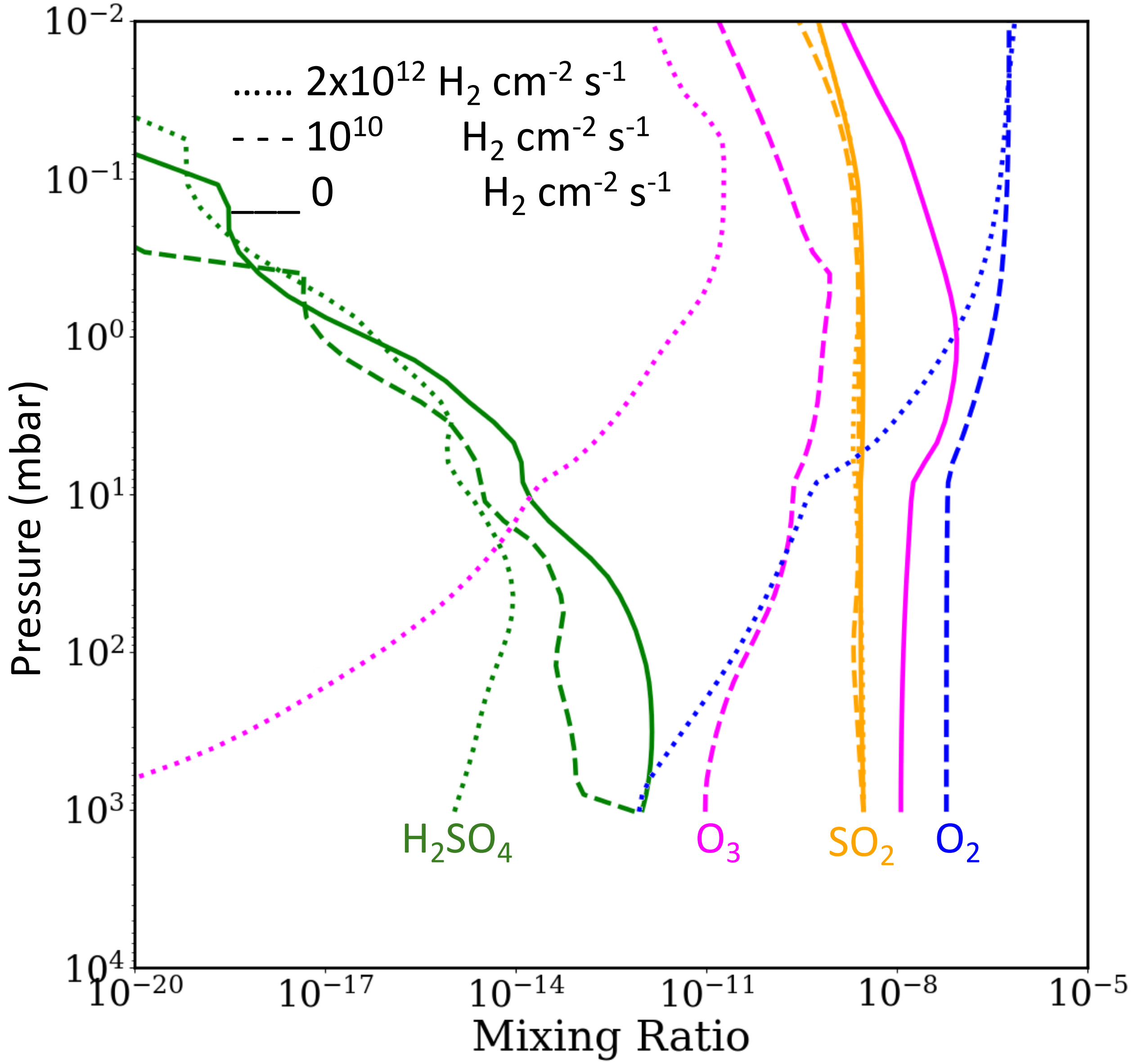

NASA/JPL



Species	Abundance	Ref
S Group		
SO_2	0.3 – 2.0 wt%	3
SO_3	3.3 – 5.5 wt% 0.1 – 12 wt%	3 1
H_2S	22 – 76 ppm 0.003 – 0.017 wt%	3 1
N Group		
NO_3^-	168 – 277 ppm 0.01 – 0.065 wt% 12 – 579 nmol (NO reported)	3 1 2
HCN	ND – 83 nmol	2
ClCN	ND – 2.9 nmol	2

[1] Sutter et al. (2017) [2] Stern et al. (2015)
[3] Stern et al., (2018)

1 bar 90% CO_2 10% N_2 atmosphere

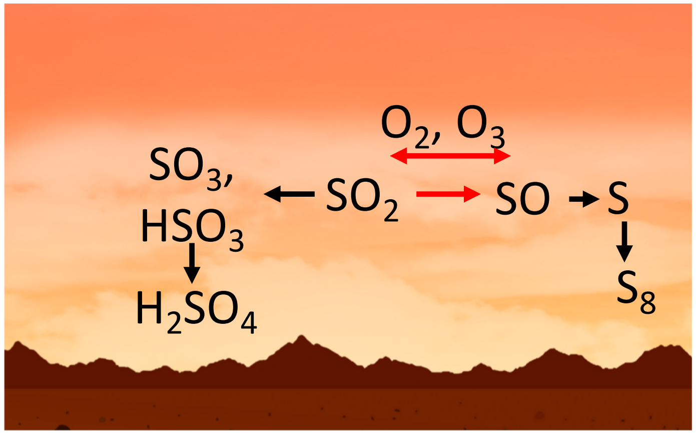


H_2SO_4 Deposition Rate:

_____ 6.4% ^{33}S enrichment

- - - 7.4% ^{33}S enrichment

..... 18.1% ^{33}S enrichment



H_2SO_4 : H_2S deposition scales with interior oxygen fugacity NOT atmospheric redox.

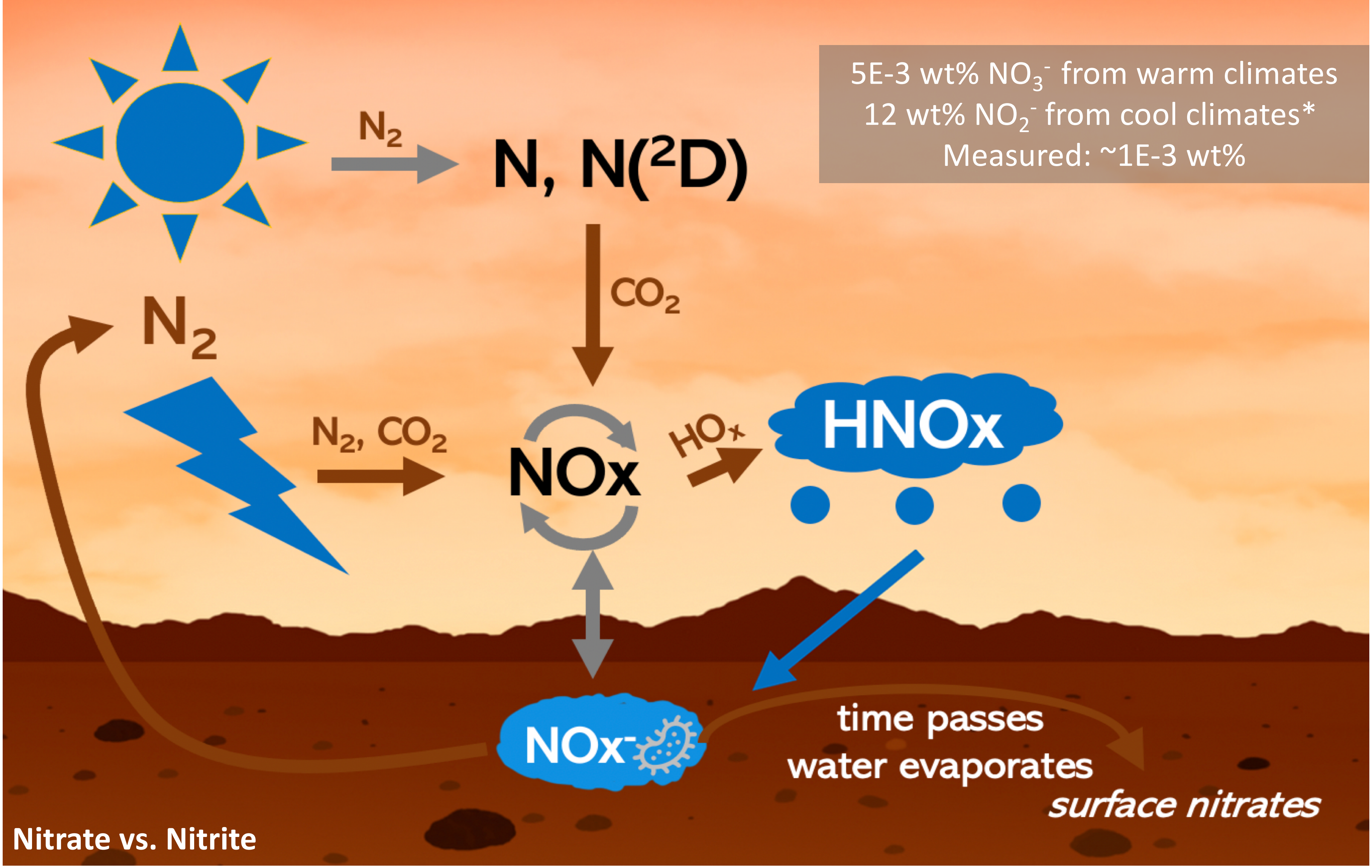
Adams, Smith, et al., in prep a

2% error floating around (lack of $^{33}S_2$? Or wrong k for a ^{33}S reaction?)
Polysulfur chemistry is ignored in these results (next step).

3. SMIF

Adams et al. (2021), *Astrobiology*
Adams et al., in review, *GRL*

5E-3 wt% NO_3^- from warm climates
12 wt% NO_2^- from cool climates*
Measured: ~1E-3 wt%



N_2 → N, $N(^2D)$

CO_2

N_2

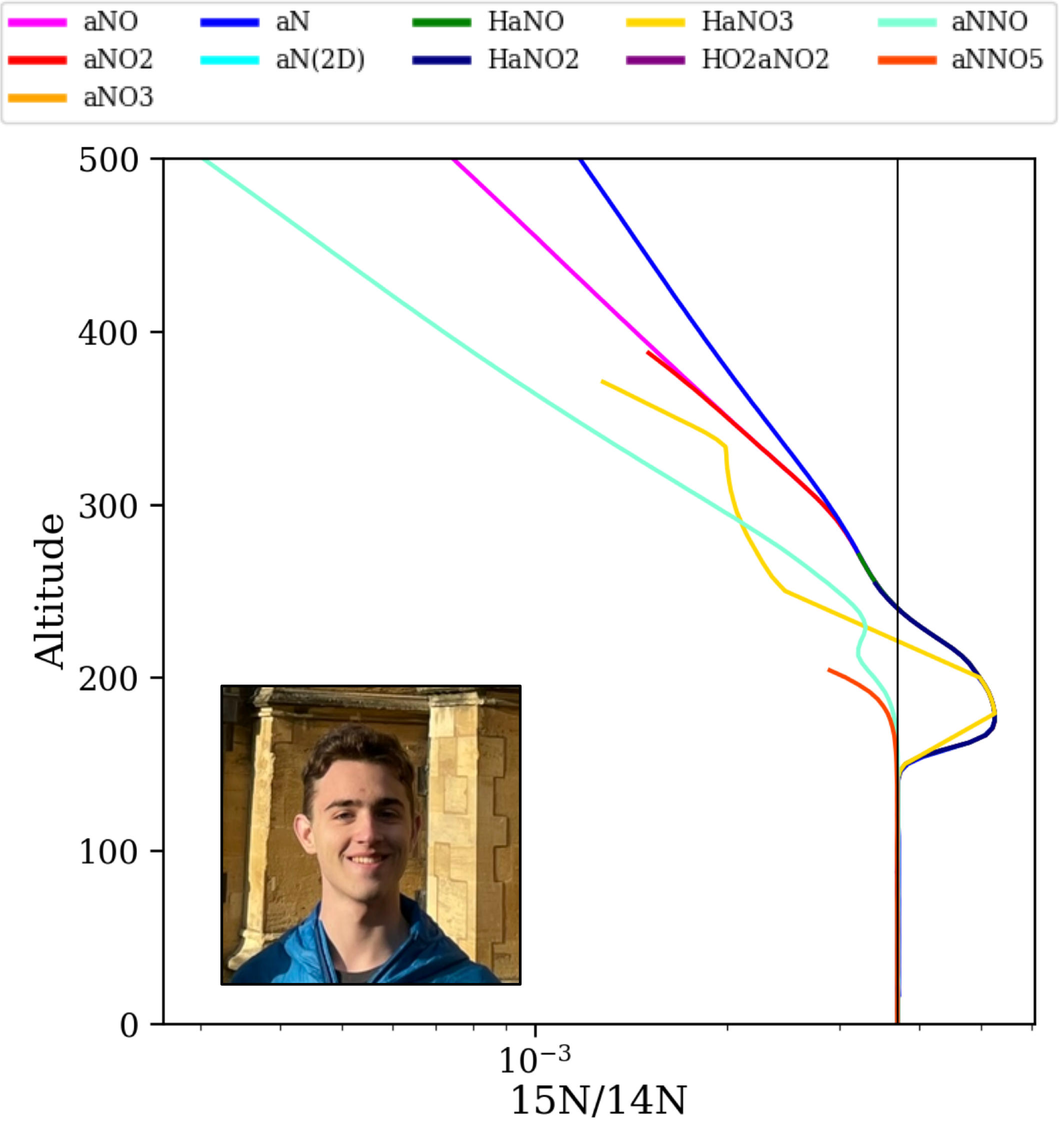
N_2, CO_2 → NOx

HO_x → HNOx

NOx^-

time passes
water evaporates
surface nitrates

Nitrate vs. Nitrite



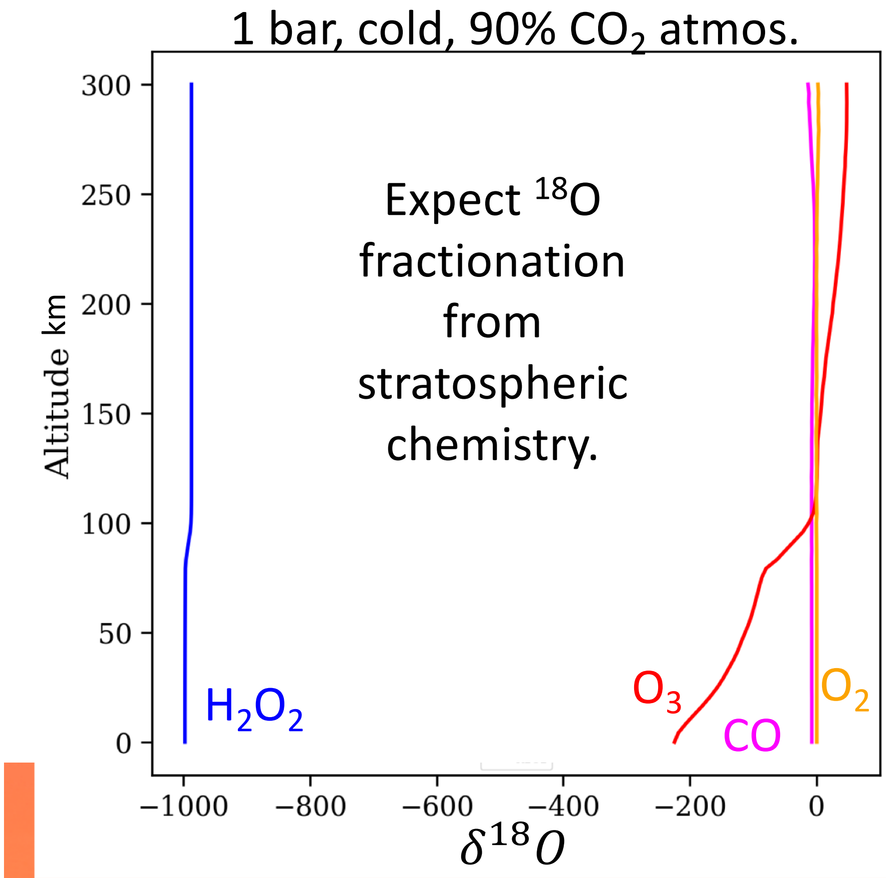
$$\delta_{15}N = \text{-1.16}$$

Changes in ^{15}N:^{14}N should track closely with atmospheric escape (ignoring surface or biologic processes)

Shawcross, Adams, Wong, et al., in prep.

>200 km, fractionation exceeds that of ^{15}N, which is unphysical!
Numerical error due to low concentrations? Or wrong k for ^{15}N-reaction?

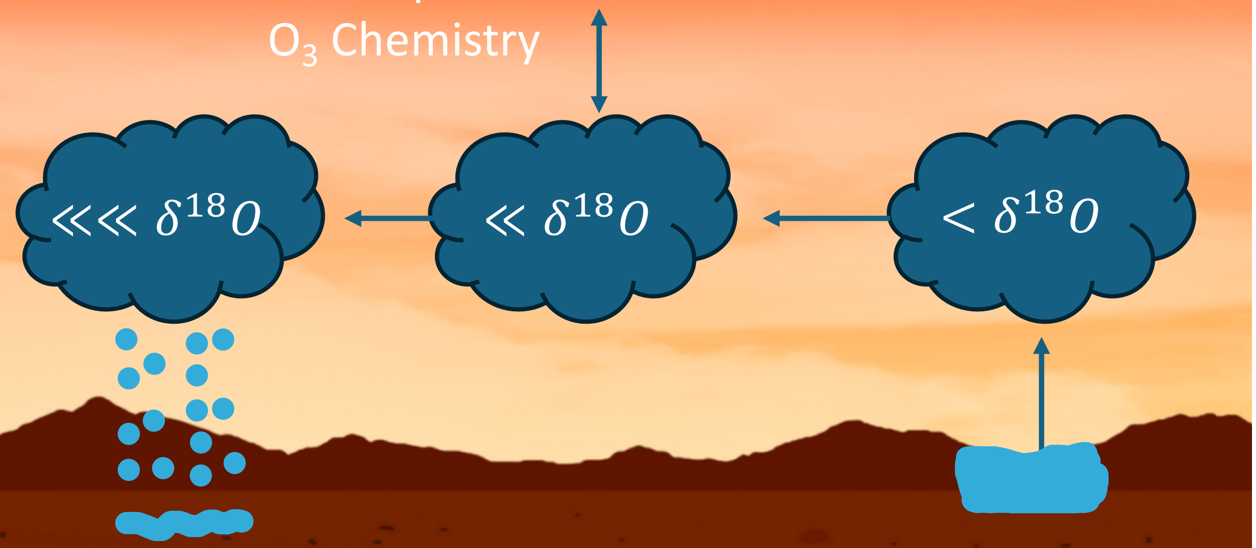
2. Age of NOx Deposition



Expect ^{18}O fractionation from stratospheric chemistry.

^{18}O fractionation will change in warm climates by preferential ^{16}O evaporation and ^{18}O condensation.
(next step)

Stratospheric O_3 Chemistry

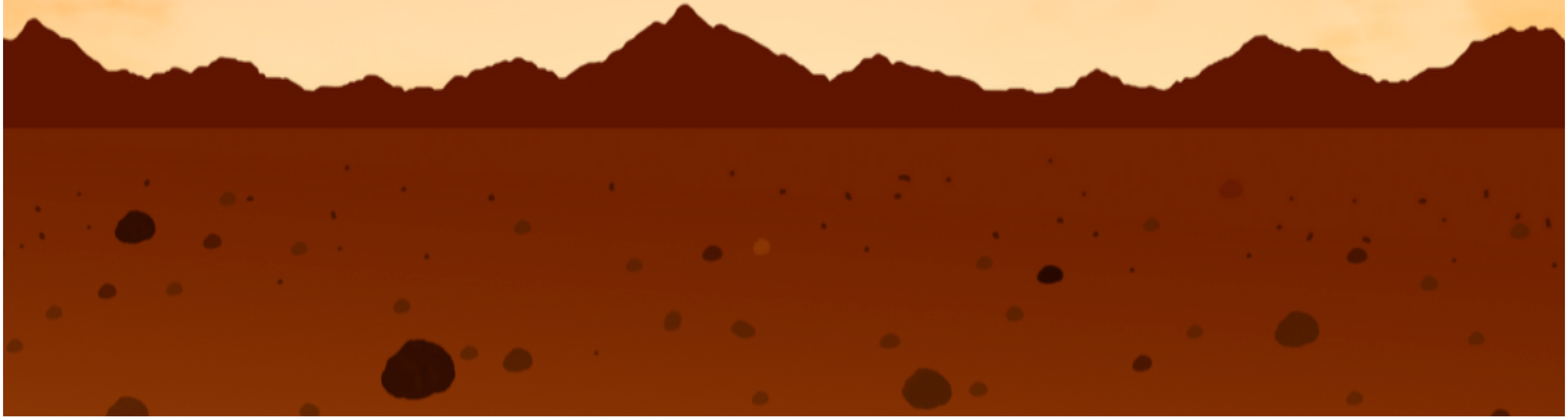


4. Rainy or Dry Climates

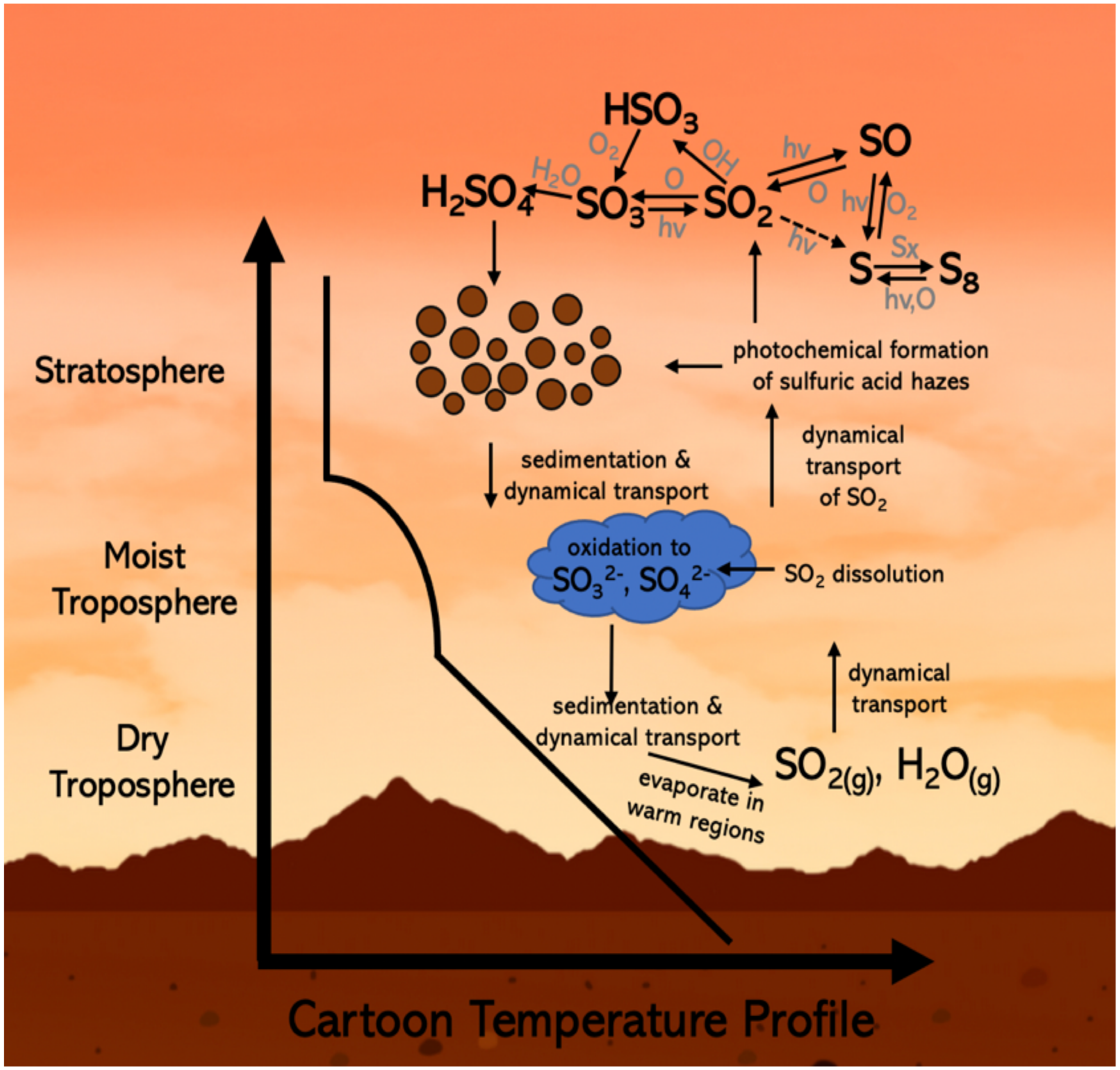
Adams, Snarr, et al., in prep b

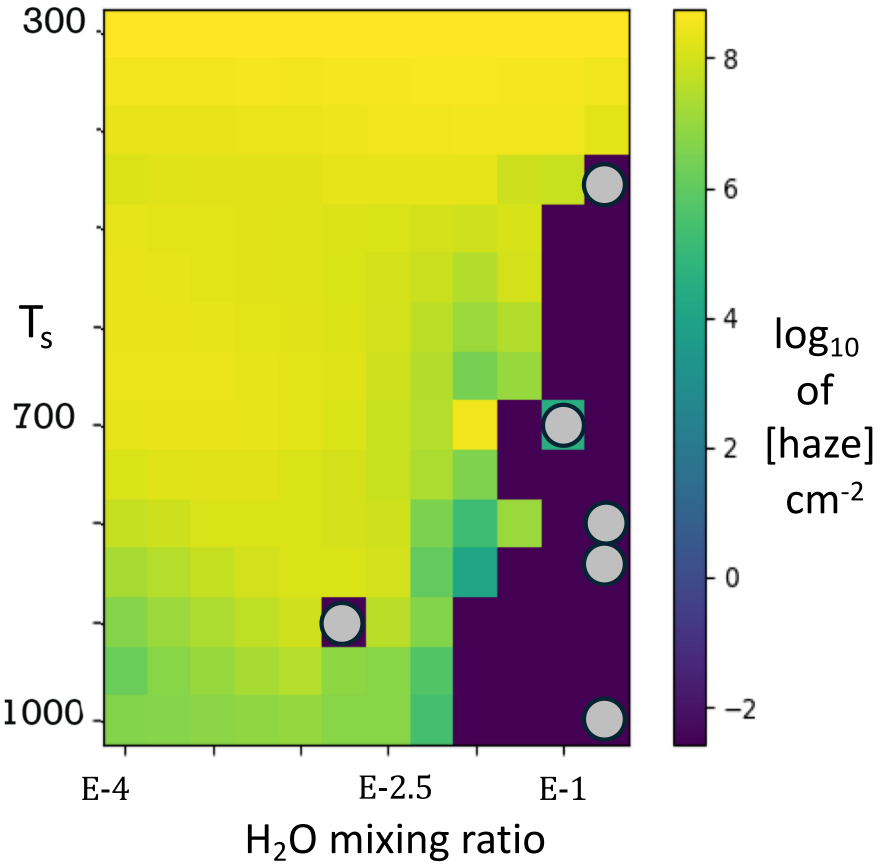
Bonus Science

- S chemistry → early Venus like worlds
- O chemistry → Snowball Earth
- N chemistry → early Earth like worlds



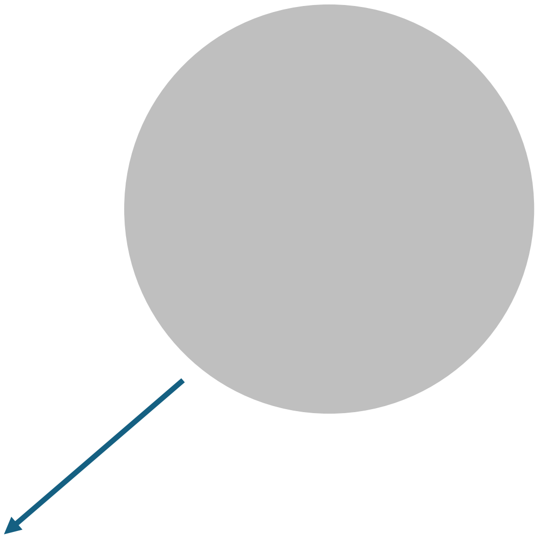
Sulfuric Acid Hazes Cool Early Venus-Like Worlds

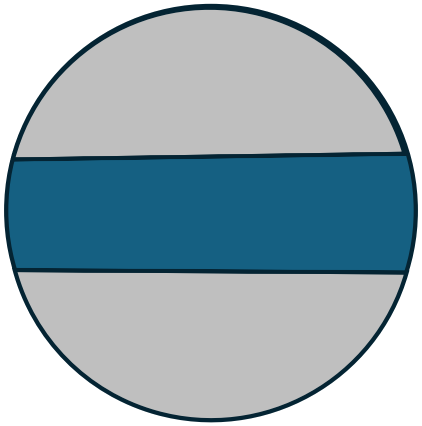




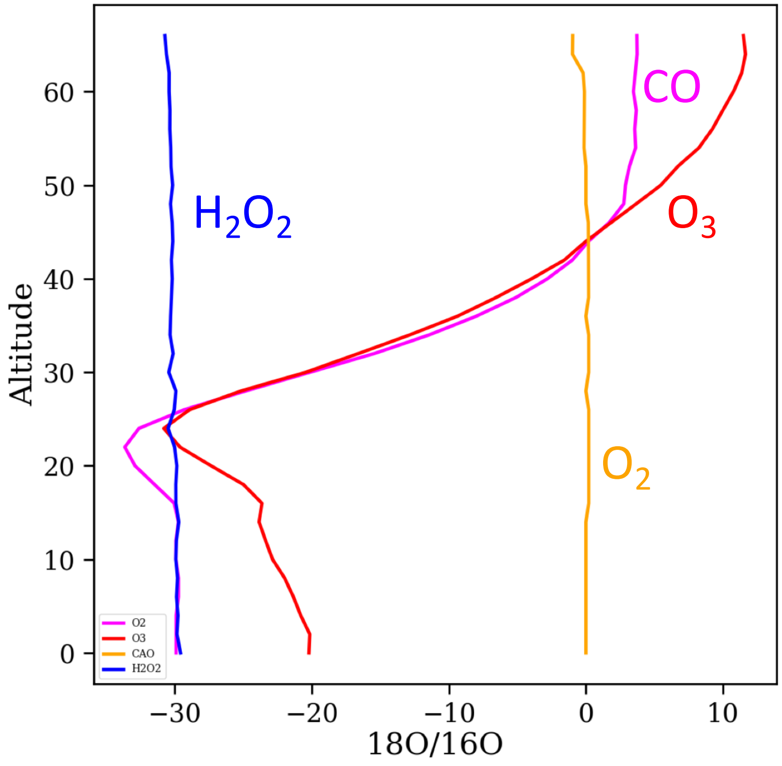
Adams et al., in prep c

Slushball
Or
Snowball Earth?





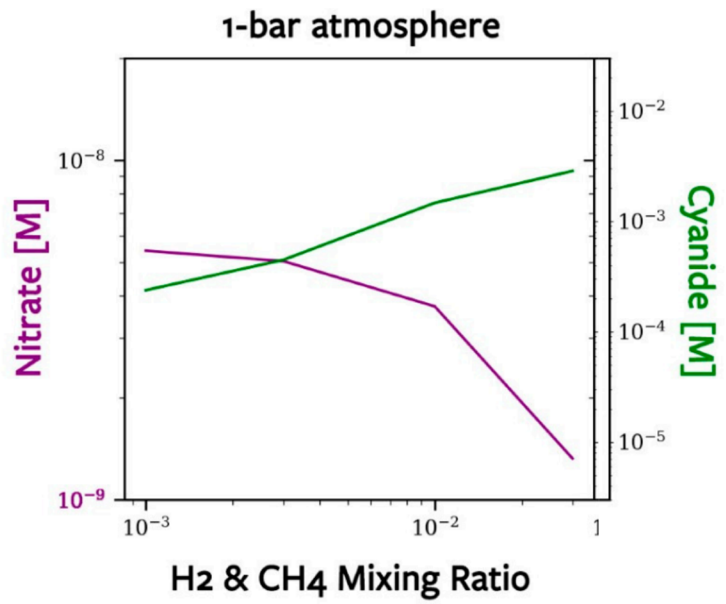
Atmosphere-ocean exchange



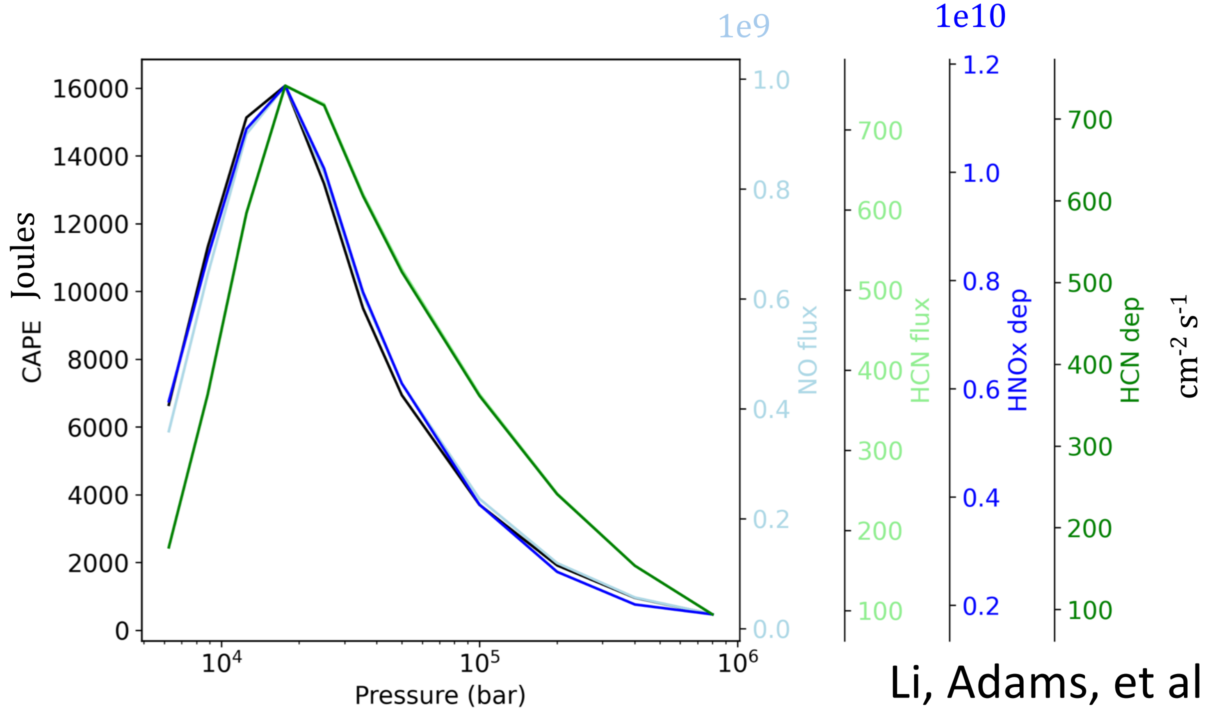
Kinetics ^{17}O model improves photochemical assumptions in Cao & Bao 2013 on ^{17}O fractionation

Snarr, Adams, et al., in prep

N-Fixation at Early Earth & Exoplanets



Christensen, Adams, Wong, et al. (2024), *Life*



Li, Adams, et al., in prep

Presented Works from the Past Year:

First Author:
1.Adams et al., in review *Nature Geoscience.* Crustal Hydration Warmed Early Mars
2.Adams et al., in review *GRL*. Nitrogen Fixation at Paleo-Mars in an Icy Atmosphere
3.Adams, Smith et al., in prep a. S-MIF at Early Mars Responds to Redox and Climate Changes
4.Adams, Snarr et al., in prep b. O-Isotope Fractionation Will Reveal Early Mars Climate Changes
5.Adams et al., in prep c. Sulfuric Acid Hazes Cool Early Venus-Like Worlds

Undergraduate Mentee Works:
6.Smith, Adams, et al., in prep for resubmission. Sensitivity study of HOx Uncertainties at Mars.
7.Thomas, Adams, et al. in prep. Hydrocarbon Chemistry at Early Mars: a Warming Solution?
8.Shawcross, Adams, Wong, et al. in prep. Nitrogen Isotope Fractionation at Early Mars
9.Snarr, Adams, et al, in prep. O-Isotope Photochemistry for Snowball Earth Interpretations
10.Christensen, Adams, Wong et al. (2024), *Life.* New Estimates of Nitrogen Fixation on Early Earth
11.Li, Adams, et al., in prep. N-Fixation at Exoplanets: P, T, and Redox Dependences.

Mastcam onboard Curiosity

Questions