This presentation participates in OSPP

Outstanding Student Poster & PICO Contest

Numerical prediction of the effects of solar energetic particle precipitation on the Martian atmospheric chemical composition

Yuki Nakamura[1,2], Naoki Terada[1], Francois Leblanc[2], Hiromu Nakagawa[1], Shotaro Sakai[1,3], Sayano Hiruba[1], Ryuho Kataoka[4,5], and Kiyoka Murase[4,5]

[1]Graduate School of Science, Tohoku University, Sendai, Japan
[2]LATMOS/CNRS, Sorbonne Université, Paris, France
[3]Planetary Plasma and Atmospheric Research Center, Graduate School of Science, Tohoku University, Sendai, Japan
[4]National Institute of Polar Research, Tokyo, Japan
[5]The Graduate University for Advanced Studies, SOKENDAI, Kanagawa, Japan

Introduction: Solar energetic particles (SEPs)

Solar Energetic Particles (SEPs)

- High energy particles (electron, proton and heavy ions) coming from the sun (few tens of keV - few GeV) associated with solar flares and coronal mass ejections.

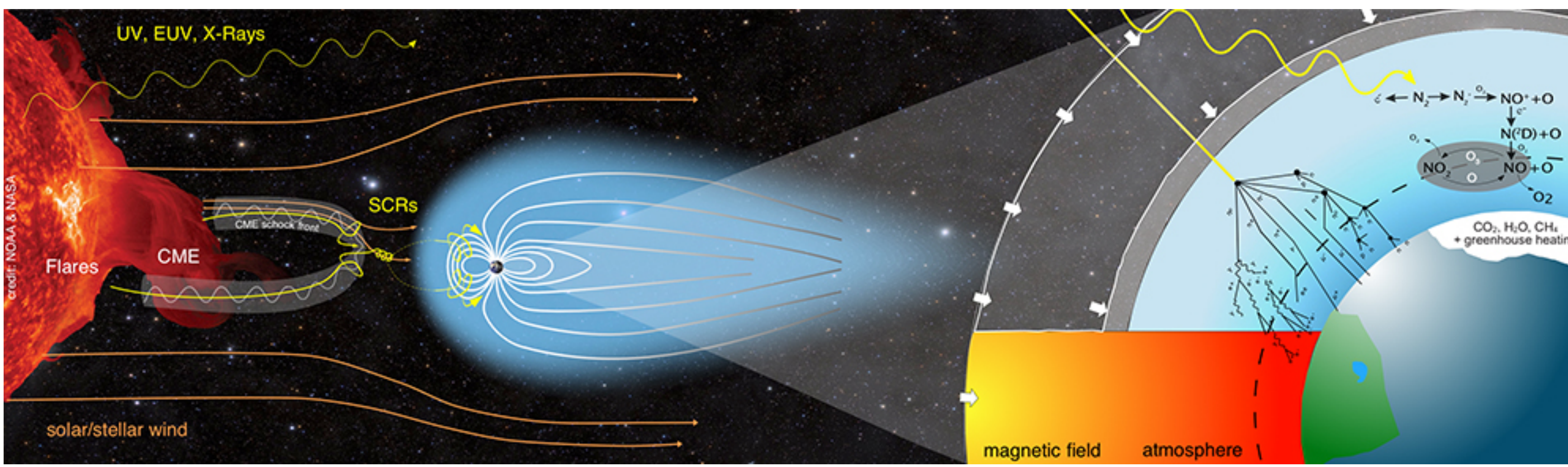
[Reams, 1999]

Effects of SEPs on planetary atmospheres

- Increased ionization of atmospheric molecules
- Increased dose rate [Kataoka and Sato, 2015]
- Auroral emissions [Sandford, 1961; Schneider et al., 2015]

Main topic of this study

- Changes in atmospheric chemistry [Solomon et al., 1981; Airapetian et al., 2016]

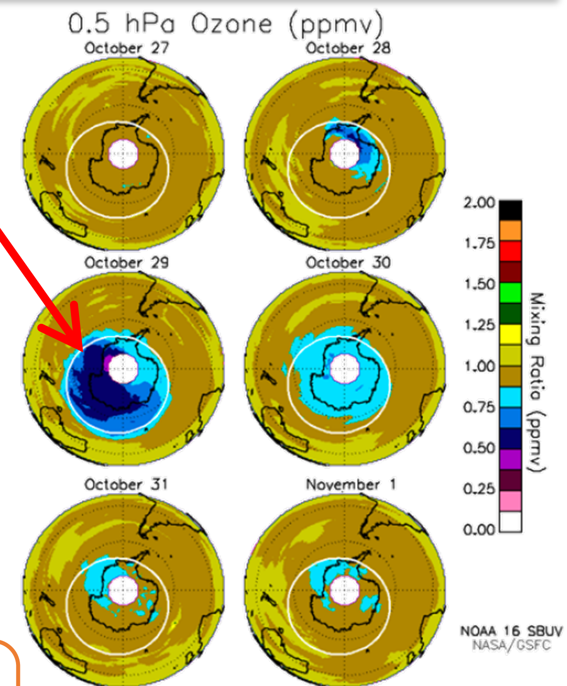


Credit: ISSI Team led by K. Herbst & J.L. Grenfell

Introduction: SEP effects on ozone at Earth

Ozone depletion [e.g. Solomon et al., 1981]

- Ozone depletion by ~40 % in the middle atmosphere at polar region during October 2003 SEP event [Jackman et al., 2005].
- Ozone destruction is caused by increases of HOx ($OH + HO_2$) and NOx ($NO + NO_2$) during SEP events [e.g. Jackman et al., 2005].



[Jackman et al., 2005]

Solar proton precipitation

O_2^+ → **Cluster ion chemistry**

$O_2^+(H_2O)$, $H_3O^+(OH)$

$H_3O^+(OH) + e^- \rightarrow H + OH + H_2O$

→ **HOx catalytic destruction cycle**

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + O \rightarrow OH + O_2$$
$$\text{Net: } O + O_3 \rightarrow O_2 + O_2$$

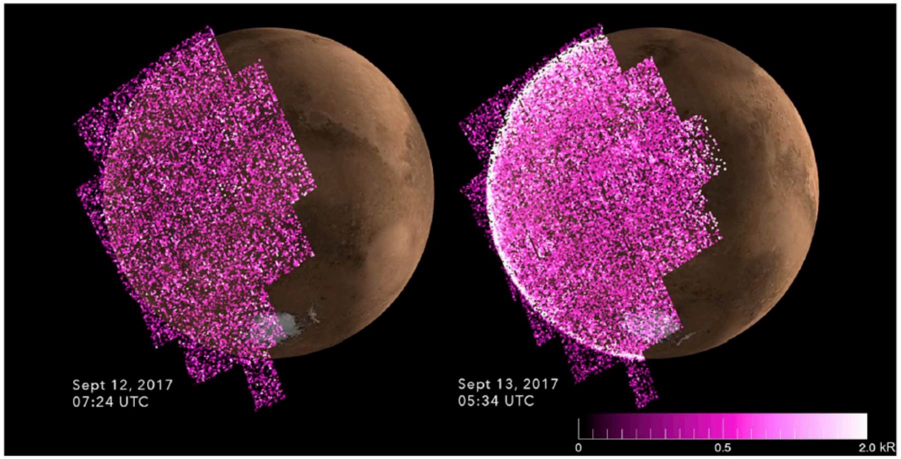
N_2^+, N, $N(^2D)$ → **Neutral chemistry**

$N(^2D) + O_2 \rightarrow NO + O$

→ **NOx catalytic destruction cycle**

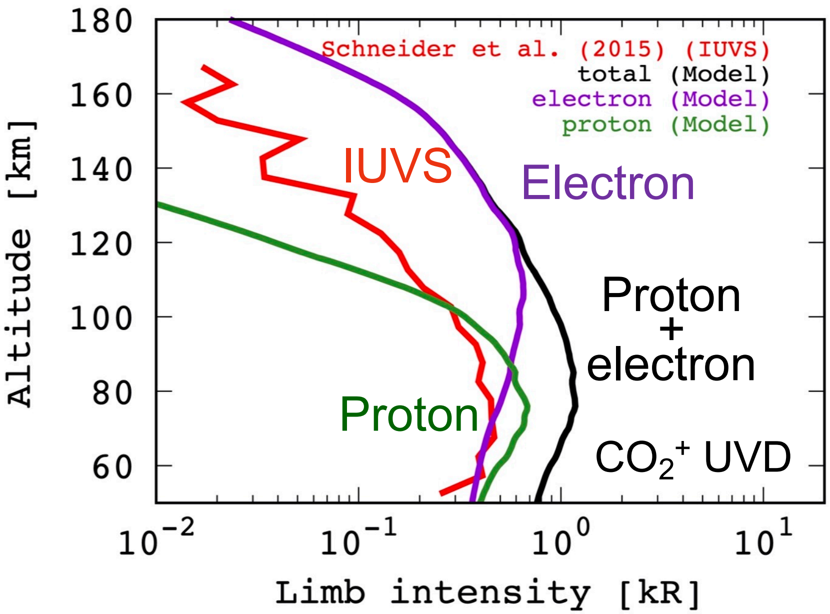
$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$\text{Net: } O + O_3 \rightarrow O_2 + O_2$$

Introduction: SEP effects on the atmosphere of Mars



[Schneider et al., 2018]

Dec. 2014 SEP event



[Nakamura et al., 2022]

Global diffuse aurora

- MAVEN/IUVS have discovered global diffuse aurora spanning across nightside of Mars during SEP events [Schneider et al., 2015].
- Emission peak at low altitude (~70 km [Schneider et al., 2015; 2018].
- Both SEP electrons and protons contributed to the diffuse auroral emission [Nakamura et al., 2022].

Effects on atmospheric chemistry?

- **There is no understanding of the SEP effects on the atmospheric chemistry of Mars.**
- Trace Gas Orbiter (TGO) is expected to detect changes in chemical compositions during SEP events in several years of increasing phase of solar cycle 25.

Purposes

To investigate the effects of SEPs on atmospheric chemistry of Mars.
To evaluate the detectability of chemical species.

We have developed two numerical models:

① Particle TRansport In Planetary atmospheres (PTRIP)

Monte Carlo model of electron, proton and hydrogen atom transport in the planetary atmospheres [Nakamura et al., 2022].

② General photochemical model

Designed for adaptability to many planetary bodies (Mars, Jupiter, Earth, Titan, etc.) and flexibility to add/remove/modify chemical reactions by using Python GUI and photochemical calculation routine written in Fortran.

Model: Particle TRansport In Planetary atmosphere (PTRIP)

PTRIP: Monte Carlo model

[Nakamura et al., 2022]

- In PTRIP, equations of motion are solved for each incident particle.
- Random numbers are used for collisional processes.

Collision probability:

$$P_i = 1 - \exp\left[-\sum_s n_s(\boldsymbol{l})\sigma_s^T(E)\Delta l\right]$$

Collision physics

electron : ionization, excitation, dissociation, elastic

proton : ionization, electron-capture, elastic

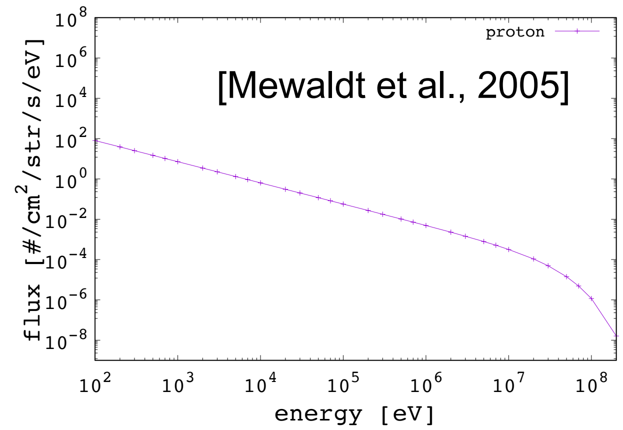
H atom : ionization, charge-stripping, elastic

Energy range proton: 100 eV – 200 MeV

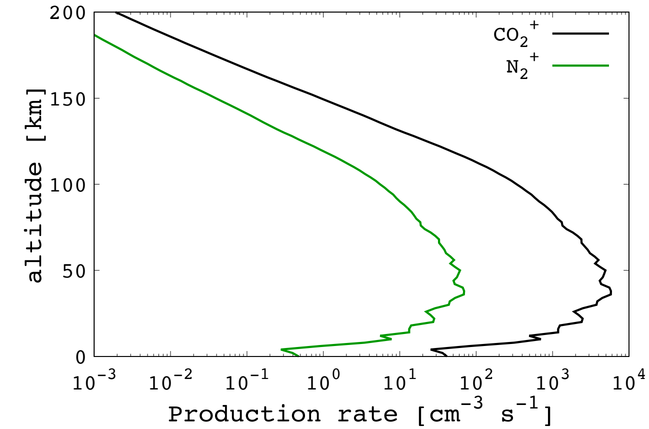
Other inputs Isotropic pitch angle

SEP proton input fluxes

- SEP event on 28 Oct. 2003 "Halloween event"



- Calculated ionization rate:



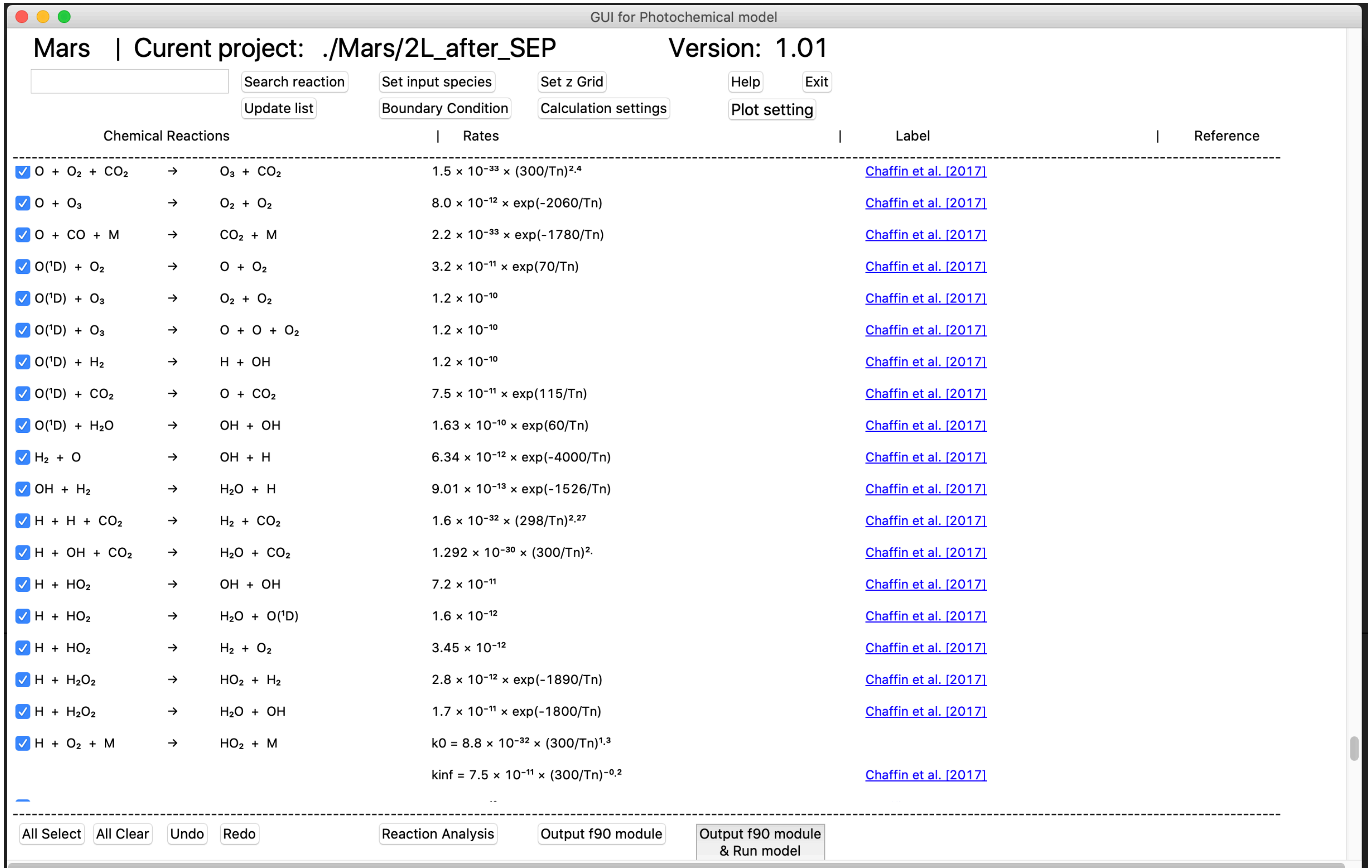
- $N_2^+ : N^+ : N : N(^2D) = 1 : 0.22 : 0.73 : 0.95$

[Krasnopolsky, 2009]

Model: General photochemical model

Python GUI + Fortran routine

Designed for adaptability to many planetary bodies (Mars, Jupiter, Earth, Titan, etc.) and flexibility to add/remove/modify chemical reactions by using Python GUI and photochemical calculation routine written in Fortran.



Chemical Reactions			Rates	Label	Reference
$O + O_2 + CO_2$	→	$O_3 + CO_2$	$1.5 \times 10^{-33} \times (300/Tn)^{2.4}$		Chaffin et al. [2017]
$O + O_3$	→	$O_2 + O_2$	$8.0 \times 10^{-12} \times \exp(-2060/Tn)$		Chaffin et al. [2017]
$O + CO + M$	→	$CO_2 + M$	$2.2 \times 10^{-33} \times \exp(-1780/Tn)$		Chaffin et al. [2017]
$O(^1D) + O_2$	→	$O + O_2$	$3.2 \times 10^{-11} \times \exp(70/Tn)$		Chaffin et al. [2017]
$O(^1D) + O_3$	→	$O_2 + O_2$	1.2×10^{-10}		Chaffin et al. [2017]
$O(^1D) + O_3$	→	$O + O + O_2$	1.2×10^{-10}		Chaffin et al. [2017]
$O(^1D) + H_2$	→	$H + OH$	1.2×10^{-10}		Chaffin et al. [2017]
$O(^1D) + CO_2$	→	$O + CO_2$	$7.5 \times 10^{-11} \times \exp(115/Tn)$		Chaffin et al. [2017]
$O(^1D) + H_2O$	→	$OH + OH$	$1.63 \times 10^{-10} \times \exp(60/Tn)$		Chaffin et al. [2017]
$H_2 + O$	→	$OH + H$	$6.34 \times 10^{-12} \times \exp(-4000/Tn)$		Chaffin et al. [2017]
$OH + H_2$	→	$H_2O + H$	$9.01 \times 10^{-13} \times \exp(-1526/Tn)$		Chaffin et al. [2017]
$H + H + CO_2$	→	$H_2 + CO_2$	$1.6 \times 10^{-32} \times (298/Tn)^{2.27}$		Chaffin et al. [2017]
$H + OH + CO_2$	→	$H_2O + CO_2$	$1.292 \times 10^{-30} \times (300/Tn)^{2.}$		Chaffin et al. [2017]
$H + HO_2$	→	$OH + OH$	7.2×10^{-11}		Chaffin et al. [2017]
$H + HO_2$	→	$H_2O + O(^1D)$	1.6×10^{-12}		Chaffin et al. [2017]
$H + HO_2$	→	$H_2 + O_2$	3.45×10^{-12}		Chaffin et al. [2017]
$H + H_2O_2$	→	$HO_2 + H_2$	$2.8 \times 10^{-12} \times \exp(-1890/Tn)$		Chaffin et al. [2017]
$H + H_2O_2$	→	$H_2O + OH$	$1.7 \times 10^{-11} \times \exp(-1800/Tn)$		Chaffin et al. [2017]
$H + O_2 + M$	→	$HO_2 + M$	$k0 = 8.8 \times 10^{-32} \times (300/Tn)^{1.3}$ $kinf = 7.5 \times 10^{-11} \times (300/Tn)^{-0.2}$		Chaffin et al. [2017]

Model: General photochemical model

General photochemical model (1D model)

- Solving series of continuity equations by using implicit method.

$$
\begin{cases}
\dfrac{\partial n_i}{\partial t} = P_i - L_i - \dfrac{\partial \Phi_i}{\partial z} \\[2ex]
\Phi_i = -n_i D_i \left(\dfrac{1}{n_i}\dfrac{dn_i}{dz} + \dfrac{1}{H_i} + \dfrac{(1+\alpha_i)}{T}\dfrac{dT}{dz} \right) - n_i K \left(\dfrac{1}{n_i}\dfrac{dn_i}{dz} + \dfrac{1}{H} + \dfrac{1}{T}\dfrac{dT}{dz} \right) & \text{for neutrals (molecular \& eddy diffusion),} \\[2ex]
\Phi_i = -n_i D_i \left(\dfrac{1}{n_i}\dfrac{dn_i}{dz} + \dfrac{1}{H_i} + \dfrac{(1+\alpha_i)}{T}\dfrac{dT}{dz} + \dfrac{q_i}{e}\dfrac{T_e/T_i}{p_e}\dfrac{dp_e}{dz} \right) & \text{for ions (ambipolar diffusion),}
\end{cases}
$$

Calculation settings

- Surface pressure: 6 mbar CO_2
- N_2 mixing ratio: 1.9% at surface

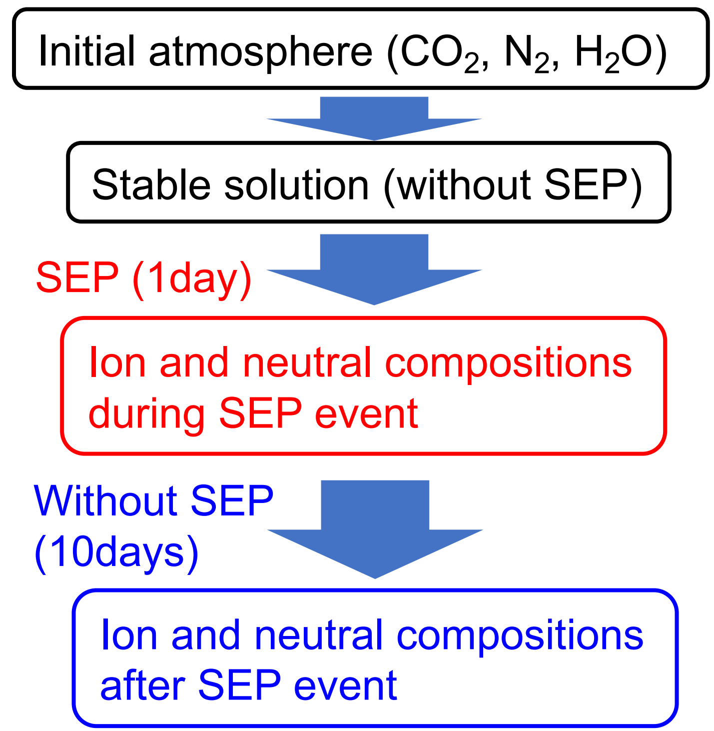
[Mahaffy et al., 2013]

- Temperature: Krasnopolsky [2010]
- Water vapor: Krasnopolsky [2010]
- H, H_2 escape: Jeans escape
- O escape flux: 1.2×10^8 [$cm^{-2}s^{-1}$]

[Chaffin et al., 2017]

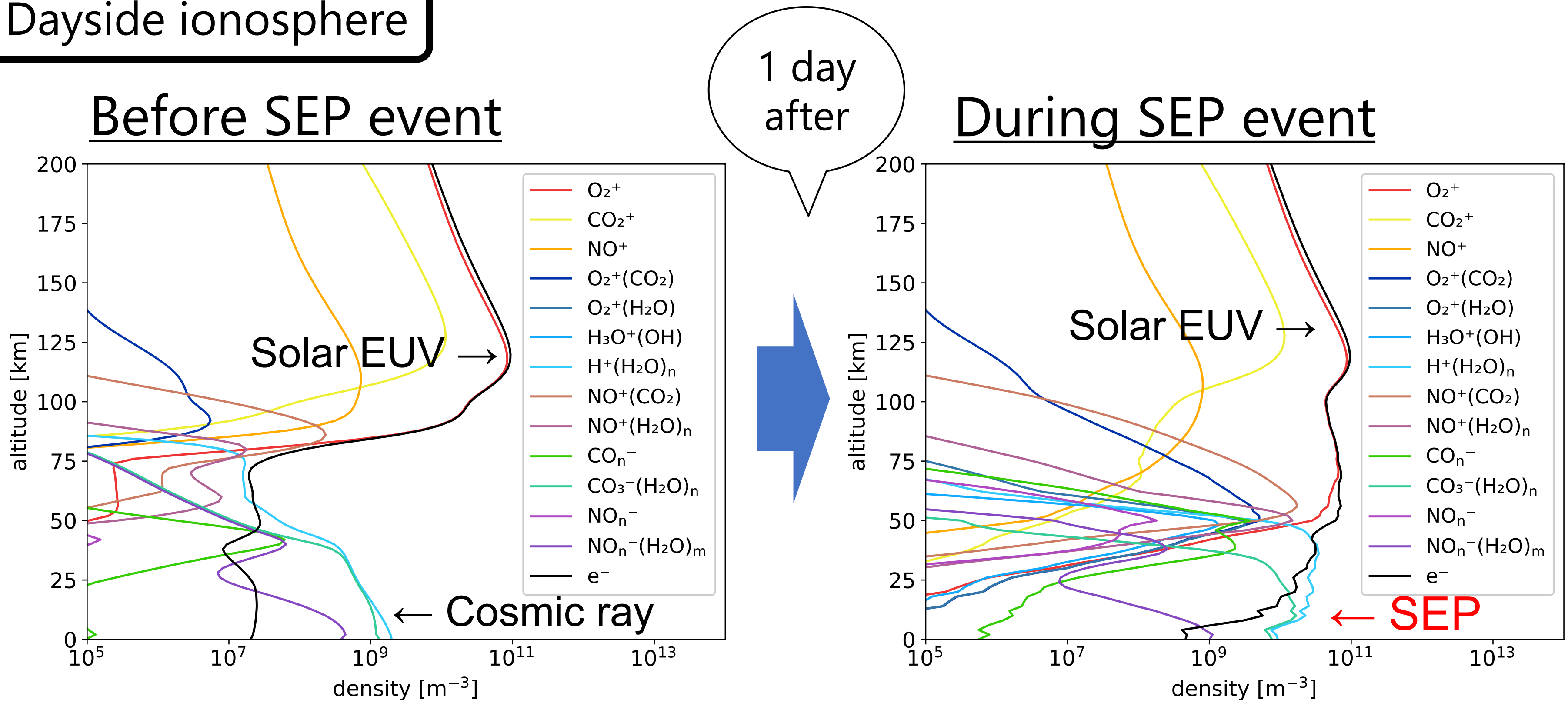
Chemical reactions (34 neutrals, 48 ions)

- 485 chemical reactions are considered.
  neutral chemistry, ion-neutral chemistry, cluster ion chemistry



Results: Ion composition

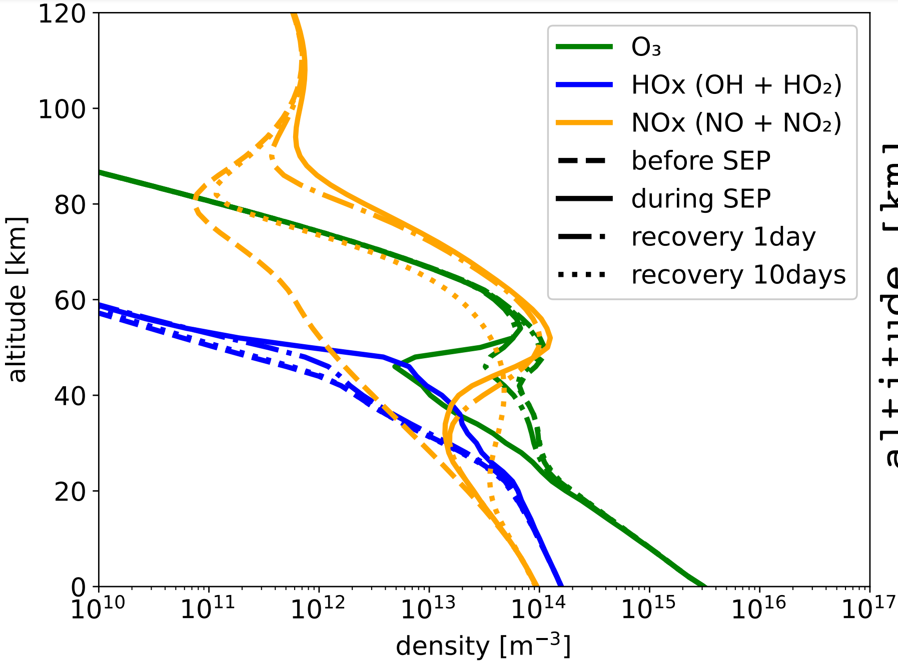
Dayside ionosphere

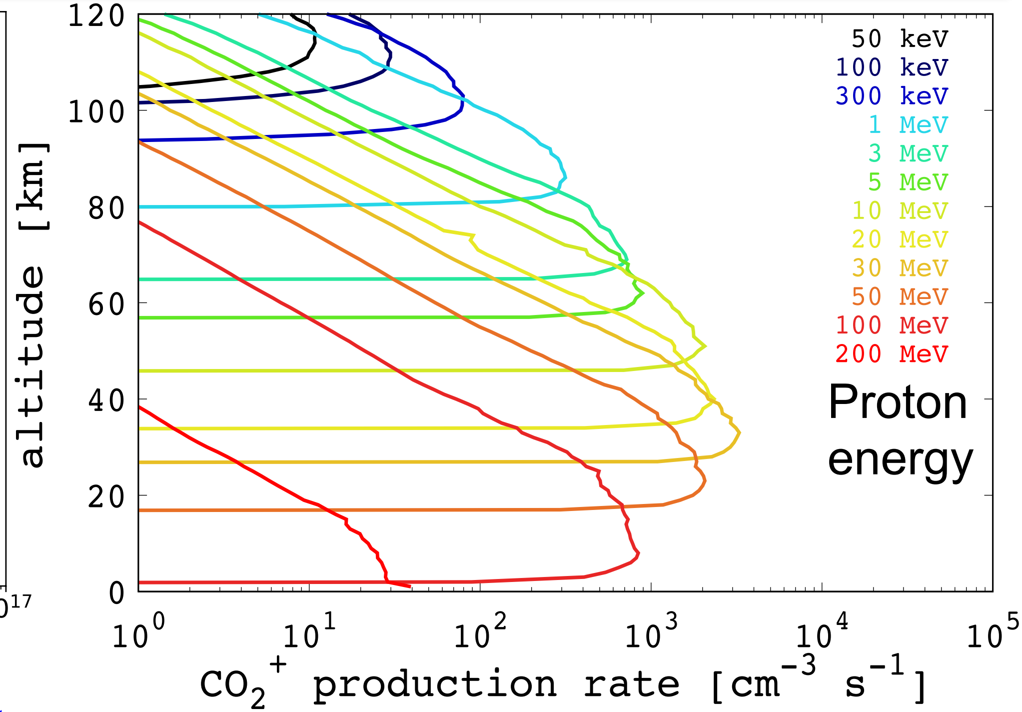


- During an extreme SEP event, ion compositions are largely altered during SEP event below 100 km altitude, producing water cluster ions ~ 10^{11} [m^{-3}] below 70 km, in agreement with a previous study [Sheel et al., 2012].

► How do neutrals change during SEP events on Mars?

Results: Changes in neutral compositions





HOx (OH + HO_2) : 5 MeV – 30 MeV proton

- **Increased** by a factor of ~5 at 20-60 km
- Almost recovered 1 day after the end of SEP event.

Ozone O_3 : 5 MeV – 30 MeV proton

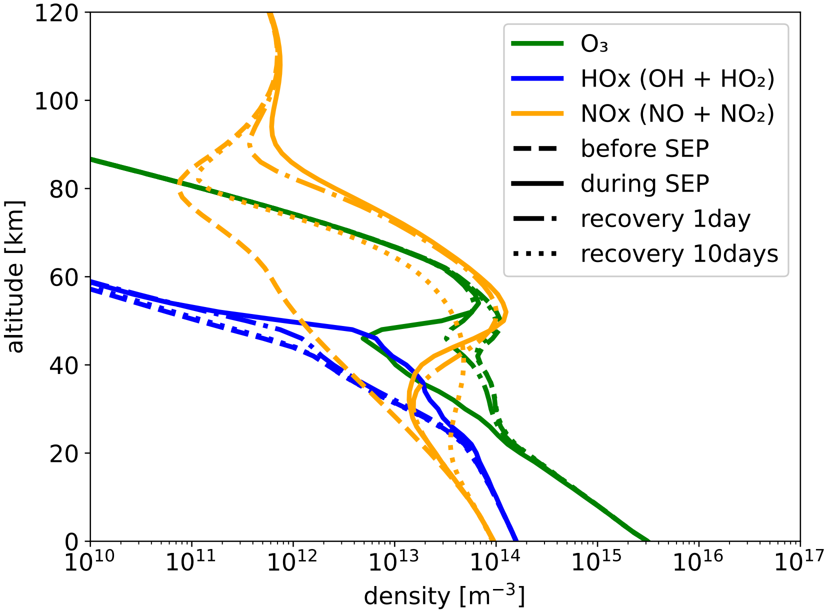
- **Decreased** by a factor of ~ 5 at 20-60 km
- Almost recovered 1 day after the end of SEP event.

NOx (NO + NO_2) : 100 keV – 30 MeV proton

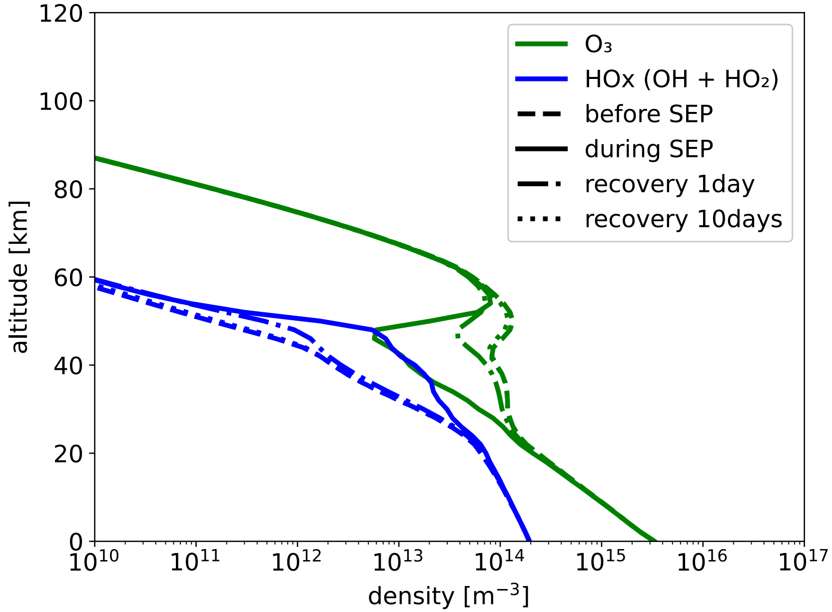
- **Increased** by a factor of ~100 at 20-100 km
- Recovery time scale is relatively long > 10 days.

Results: Changes in neutral compositions

Including all 485 reactions



Including 227 reactions except for N-related



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NOx ($NO + NO_2$): 100 keV – 30 MeV proton

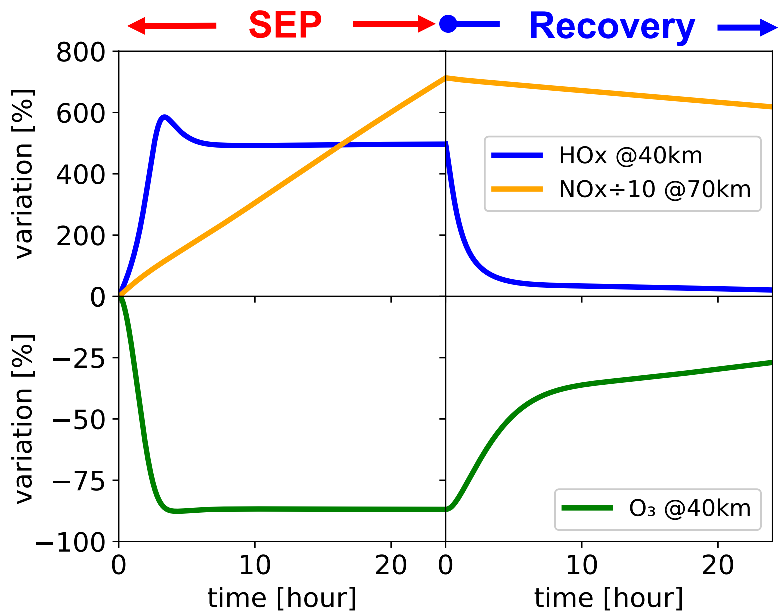
- Increased by a factor of ~100 at 20-100 km
- Recovery time scale is relatively long > 10 days.

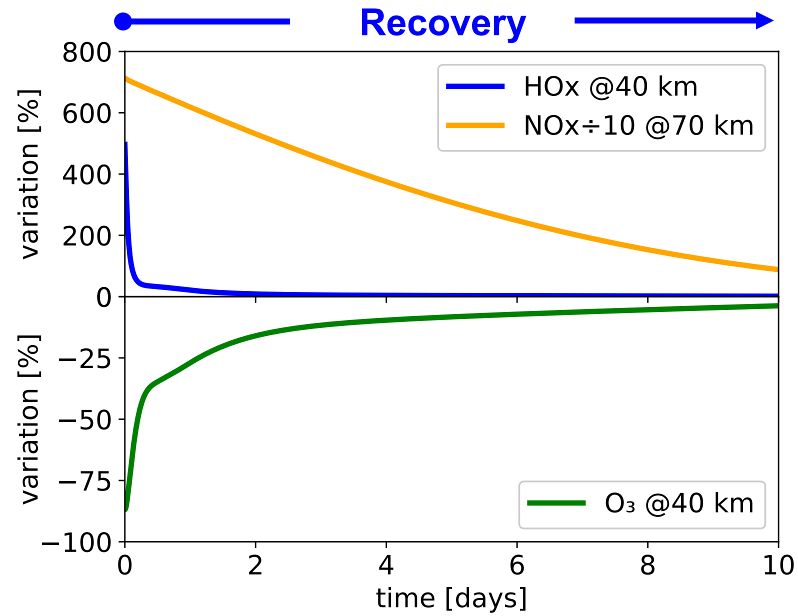
Contribution to O_3 destruction

- HOx: Effective in short-term.
- NOx: Less effective in short-term.
- Short-term ozone depletion during SEP events is driven by HOx-cycle via cluster ion chemistry.

Results: Temporal variation during and after SEP events

Temporal variation of O_3, HOx and NOx





Response time scale

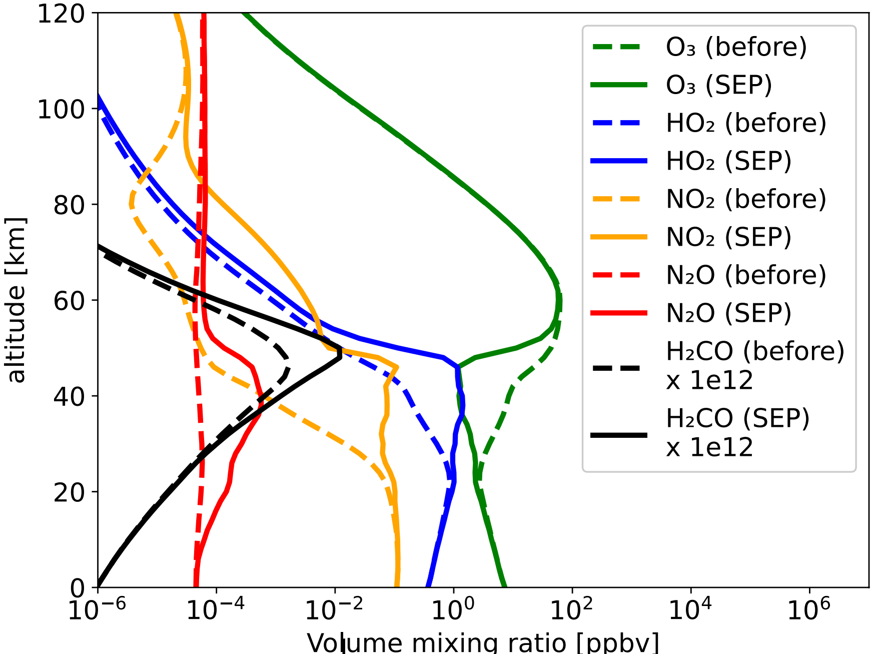
HOx and O_3 : ~ 5 hours

- Duration of SEP event does not affect enhancement of HOx and depletion of O_3.
- SEP effects quickly disappear, but slightly remain.
- Loss time scale : 10-100 sec.

NOx : ~ Several days

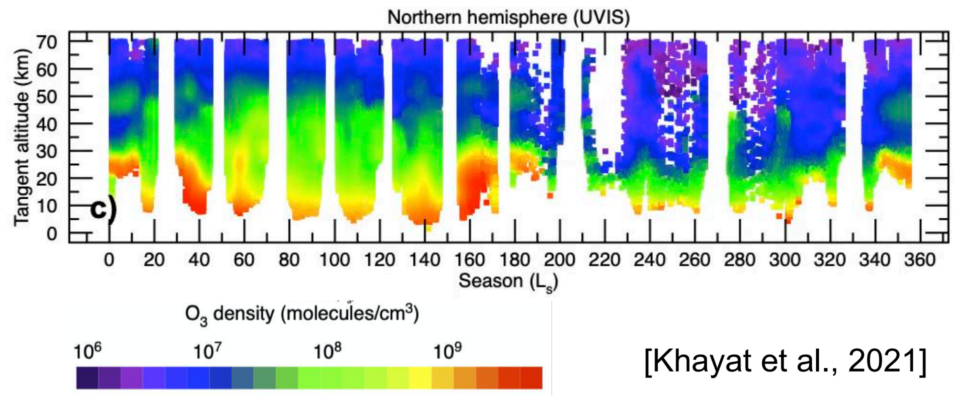
- Duration of SEP event is important in enhancement of NOx.
- SEP effects remain 10 days after.
- Loss time scale : 10^4-10^5 sec

Discussion: Detectability of chemical changes



TGO/NOMAD [Vandaele et al., 2015]

✓ High-resolution spectrometer on board Trace Gas Orbiter designed to detect atmospheric trace species.



[Khayat et al., 2021]

Species	Variability during SEP events predicted by this study	NOMAD detection limit (Solar Occultation: SO) [Vandaele et al., 2015]	Detectability
O_3	~ 10 ppb @ 20 – 50 km	0.05 ppb (UVIS, SO)	◎
HO_2	~ 1 ppb @ 20– 50 km	1 ppb (SO)	△
NO_2	~ 0.1 ppb @ 20 – 50 km	0.1 ppb (SO)	△
N_2O	~ 0.001 ppb @ 20 – 50 km	0.2 ppb (SO)	-
H_2CO	~ 1e-14 ppb @ 50 km	0.03 ppb (SO)	-

Chemical processes during SEP events on Mars

- Dominant chemical process for O_3 and HOx during SEP events

Impact ionization

R1 $CO_2 + p^* \rightarrow CO_2^+ + e^- + p^*$

Formation of cluster ions

R2 $CO_2^+ + CO_2 + M \rightarrow CO_2^+(CO_2) + M$

R3 $CO_2^+(CO_2) + O_2 \rightarrow O_2^+ + 2CO_2$

R4 $O_2^+ + CO_2 + M \rightarrow O_2^+(CO_2) + M$

R5 $O_2^+(CO_2) + H_2O \rightarrow O_2^+(H_2O) + CO_2$

R6 $O_2^+(H_2O) + H_2O \rightarrow H_3O^+(OH) + O_2$

Production of OH and H

R7 $H_3O^+(OH) + H_2O \rightarrow H^+(H_2O)_2 + OH$

R8 $CO + OH + M \rightarrow CO_2 + H + M$

R9 $H^+(H_2O)_n + e^- \rightarrow H + nH_2O$

Catalytic destruction of ozone (effective)

R10 $H + O_3 \rightarrow OH + O_2$

R11 $OH + O \rightarrow H + O_2$

- Dominant chemical process for NOx during SEP events

Impact ionization

R1 $N_2 + p^* \rightarrow N_2^+ + e^- + p^*$

R2 $N_2 + p^* \rightarrow N^+ + N(^2D) + p^*$

R3 $N_2 + p^* \rightarrow N + N(^2D) + p^*$

Neutral chemistry

R4 $N(^2D) + CO_2 \rightarrow NO + CO$

R5 $NO + N \rightarrow N_2 + O$ (> 70 km)

R6 $NO + O + M \rightarrow NO_2 + M$ (50 - 70 km)

R7 $NO + HO_2 \rightarrow NO_2 + OH$ (0 - 50 km)

R8 $N + NO_2 \rightarrow N_2O + O$

Catalytic destruction of ozone (less effective)

R9 $NO + O_3 \rightarrow NO_2 + O_2$

R10 $NO_2 + O \rightarrow NO + O_2$

Summary

- Changes in atmospheric compositions during SEP events on Mars are investigated by using PTRIP and a general photochemical model.

- **Ozone depletion by a factor of 5** could be expected during SEP events due to the precipitation of **5-30 MeV protons.**

- Duration of SEP event does not affect variation of HOx and ozone, but it affects enhancement of NOx.

- Variation of **ozone can be detected by TGO/NOMAD**, HO_2 and NO_2 are just around detection limit, whereas N_2O and H_2CO are not expected to be detected.