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Earth and Atmospheric Sciences

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# Iron-Catalyzed Chlorine Production: Reconciling $\delta^{13}$C-CO Observations with Uncertain Methane Budget Impacts

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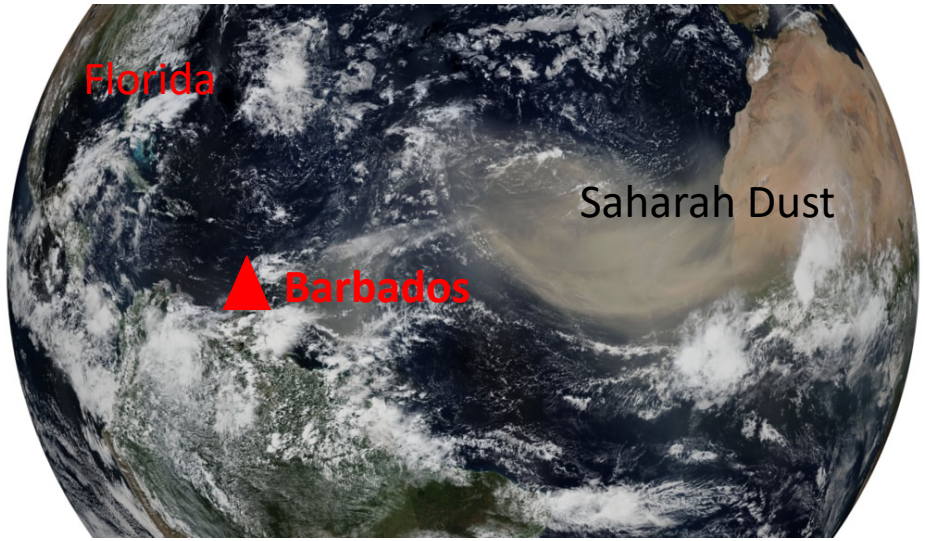
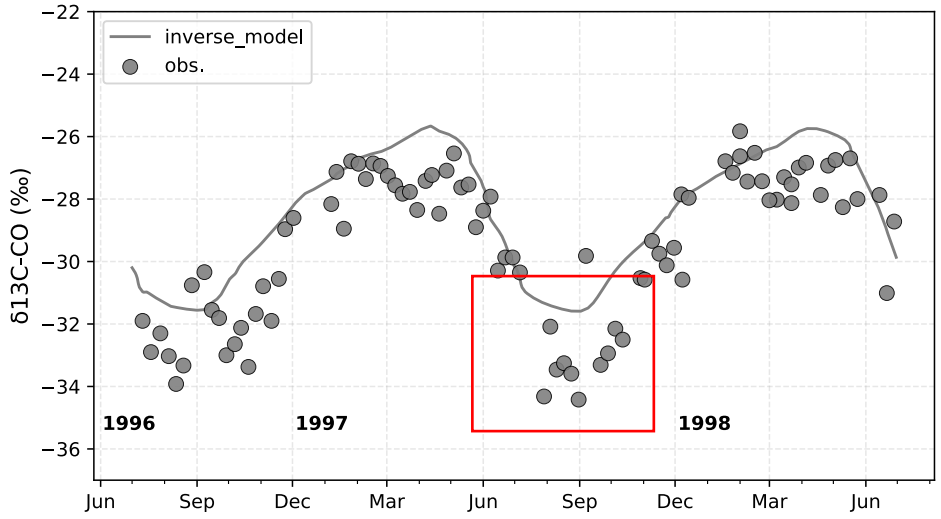
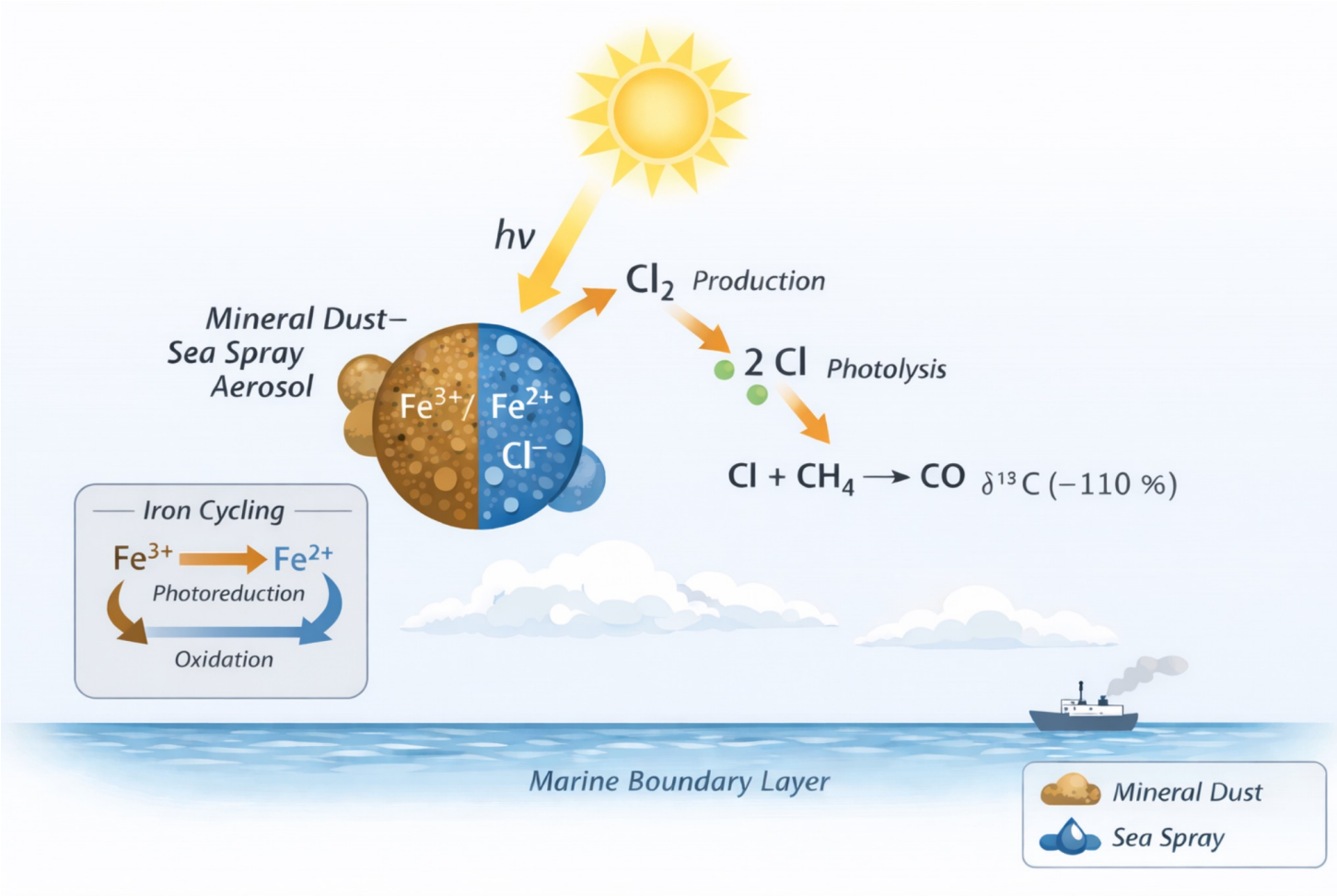
With Natalie Mahowald, Peter Hess , Daphne Meidan, John Mak

02/04/2026, NCAR winter workshop

# The missing source of chlorine: iron-catalyzed chlorine production



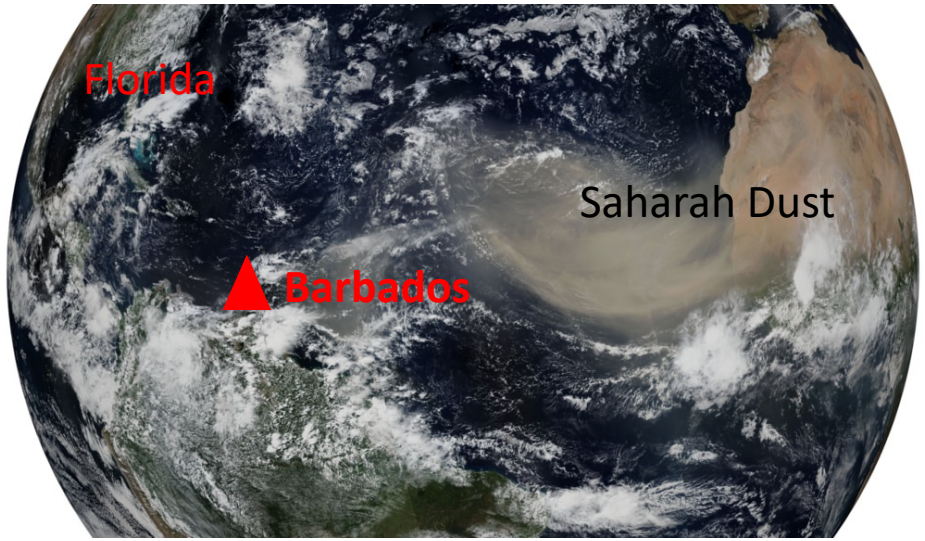



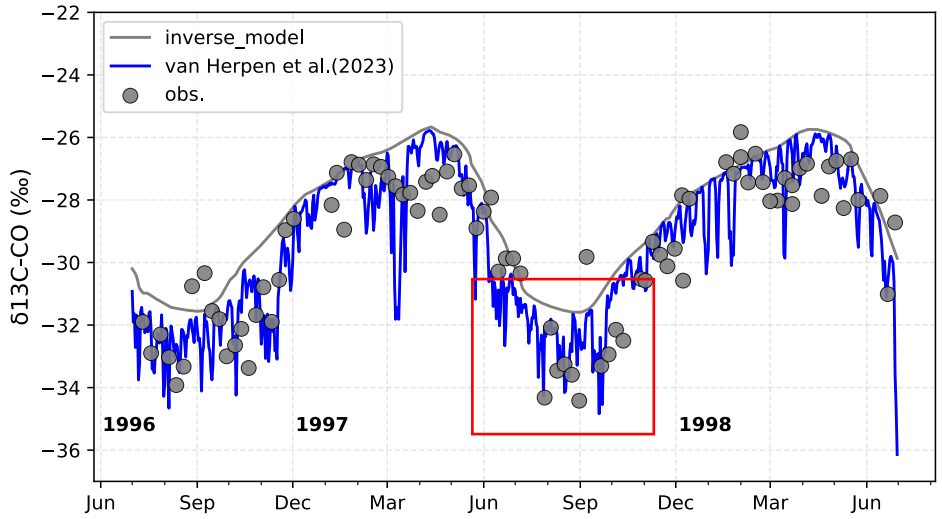



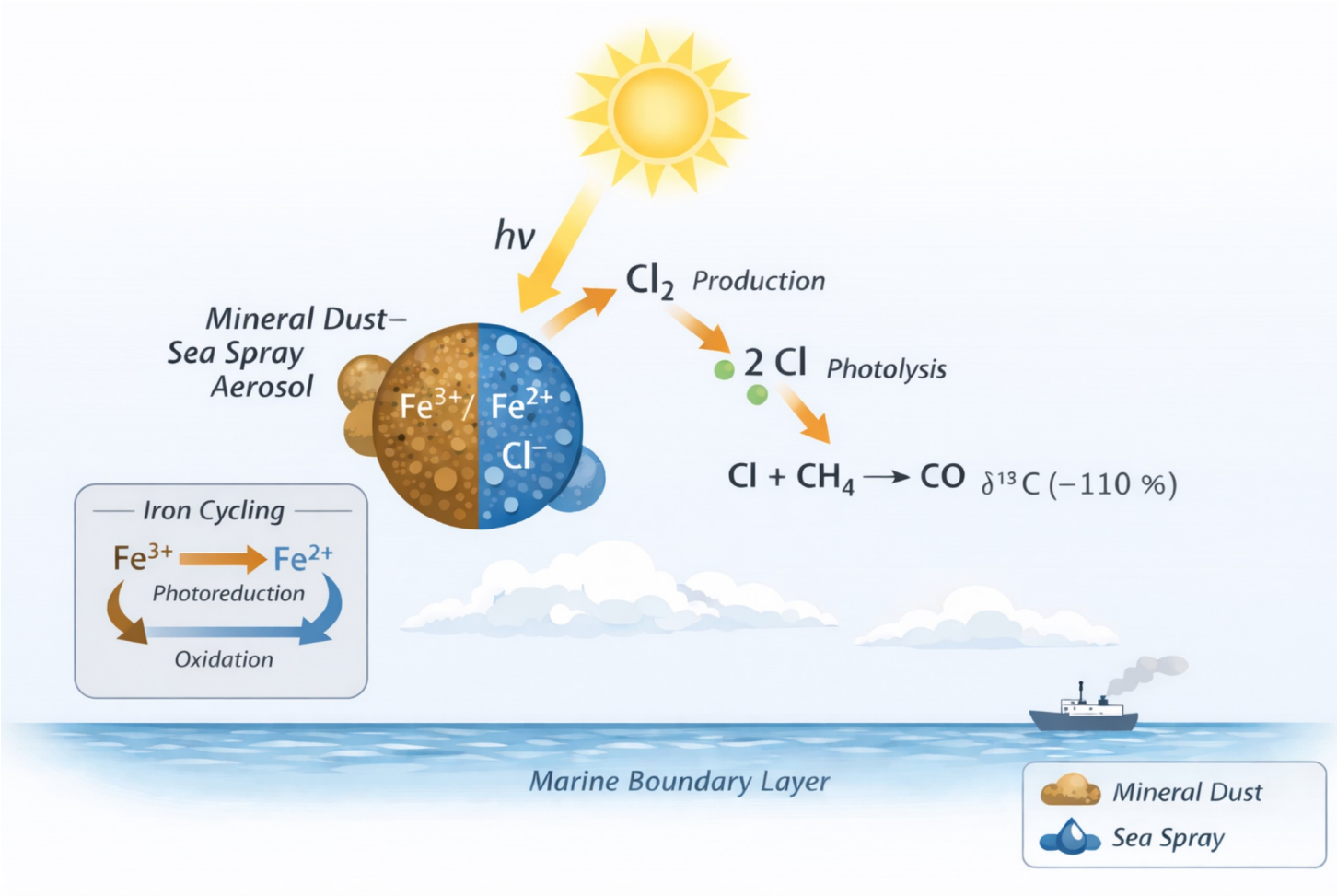

**Iron-chlorine-methane interactions**
**(Mineral Dust Sea Salt (MDSA) interactions)**

Mak et al. (2003); van Herpen et al. (2023)

# The missing source of chlorine: iron-catalyzed chlorine production




**Iron-chlorine-methane interactions**
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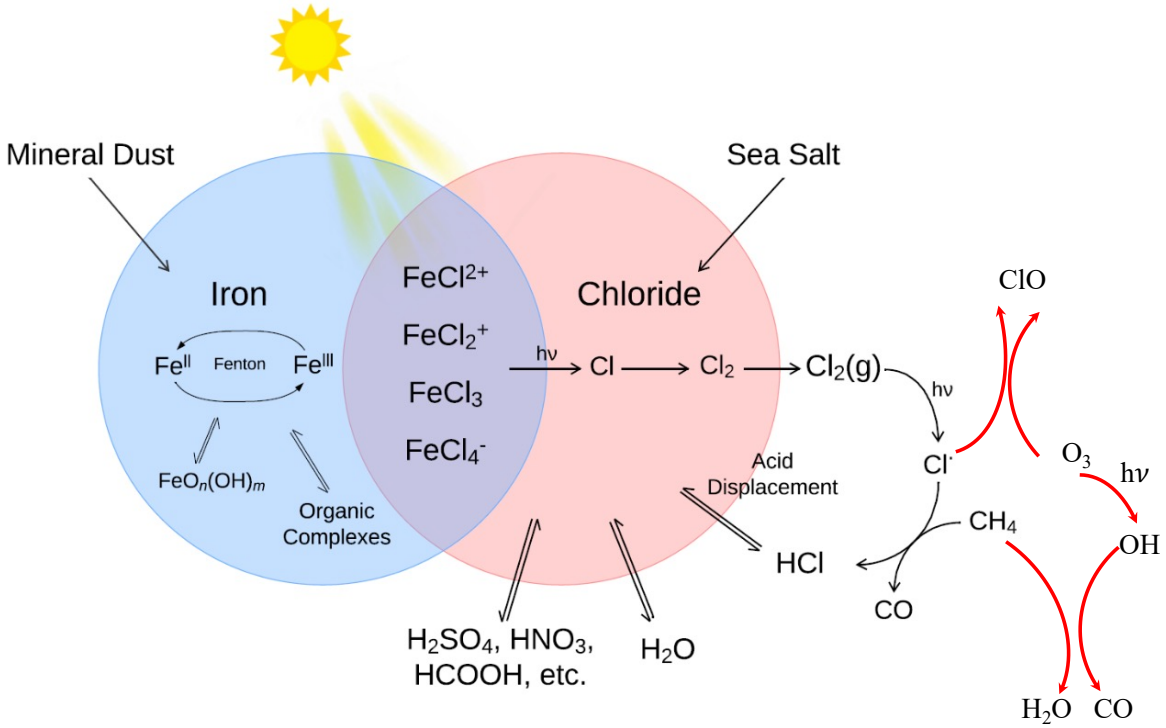
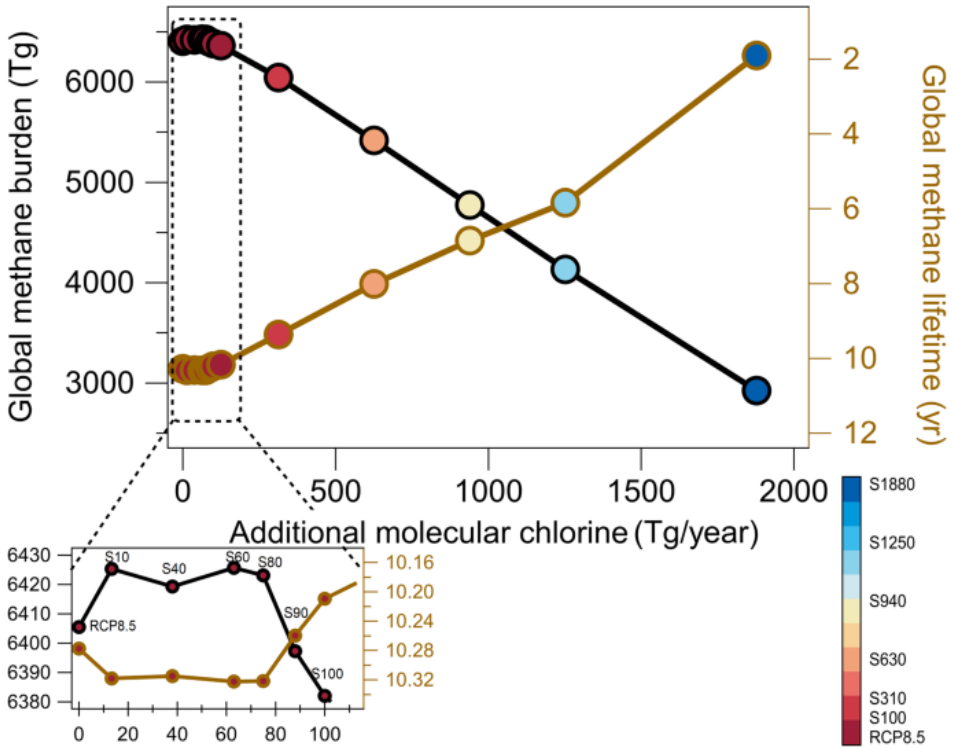
# Complex interactions between Chlorine, $CH_4$ and $O_3$




Cl reacts with $CH_4$, and also $O_3$

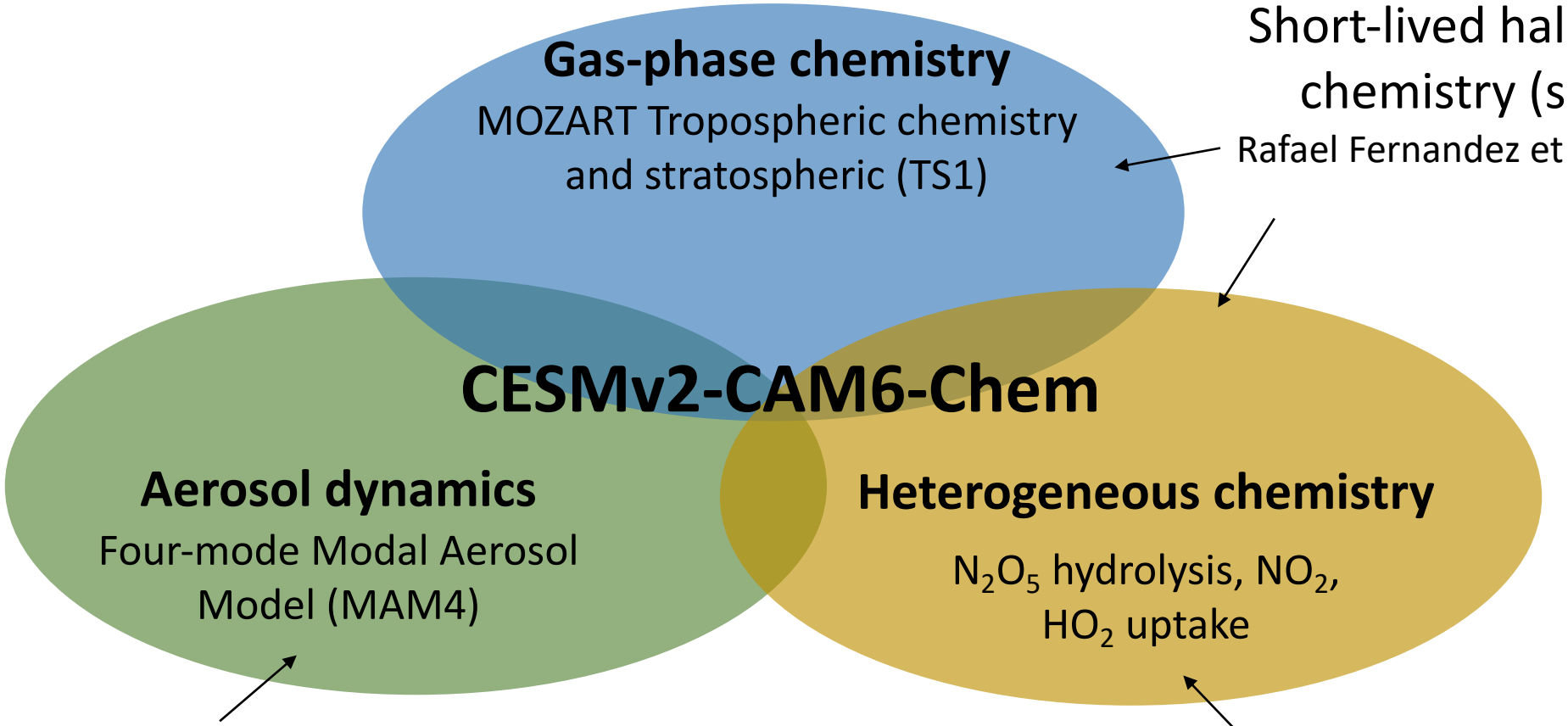



Nonlinear methane response to the adding chlorine



Mikkelsen et al. (2024);Li, Meidan et al.(2023)

# Model framework in this work: CESMv2-CAM6-Chem




Soluble iron process: Mechanism of Intermediate complexity for Modelling Iron (MIMI)
Hamilton et al. (2019)

Iron-catalyzed chlorine process (MDSA schemes)
This work

Yao et al. (to be submitted)

# Two MDSA schemes based on Lab works

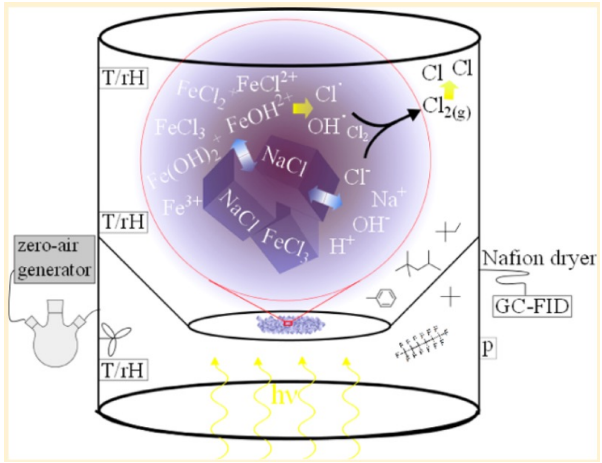
## Scheme 1: VH_M_surf scheme

Soluble iron mixing ratio

$$\frac{d[\mathrm{Cl_2}]}{dt} = \alpha_1 \chi_{\mathrm{Fe_{sol}}} l$$

Solar intensity

**Teflon smog chamber**




Wittmer et al. (2015)

❑ Reaction limited at < 900 hpa, and environment with sea salt mixing ratio > 1e-9

van Herpen et al. (2023); Meidan et al. (2024)

**CESM v1 and CESM v2 offline**

## Scheme 2: Chen scheme

Soluble iron molarity

$NO_2$ photolysis

$$\frac{d[\mathrm{Cl_2}]}{dt} = \alpha_2 [\mathrm{Fe_{sol}}][\mathrm{Cl^-}] j_{\mathrm{NO_2}} \mathrm{S}$$

Chloride molarity

Aerosol surface area

❑ No limitation on sea salt and height

Chen et al. (2024)

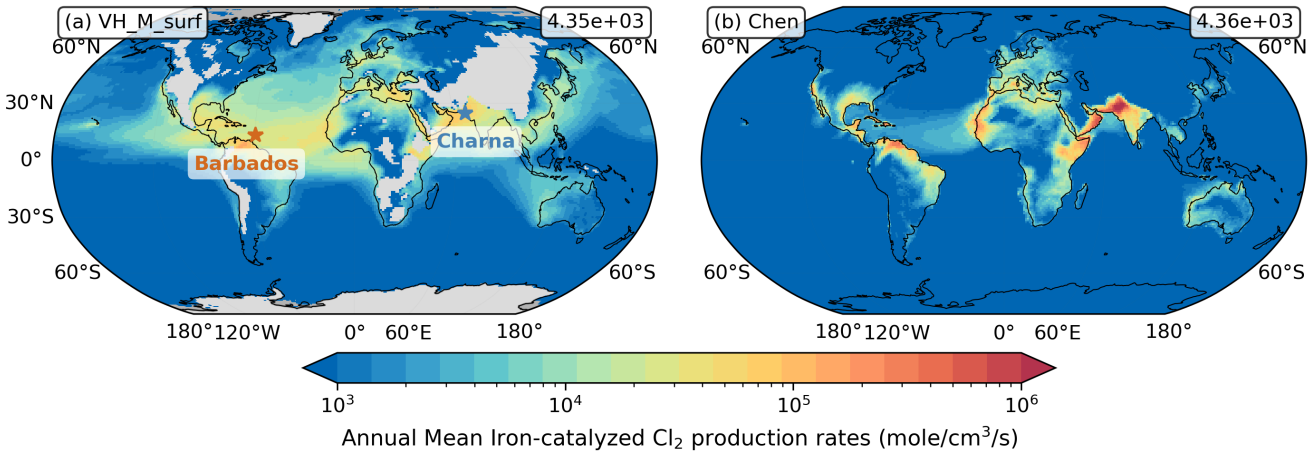
**GEOS-Chem**

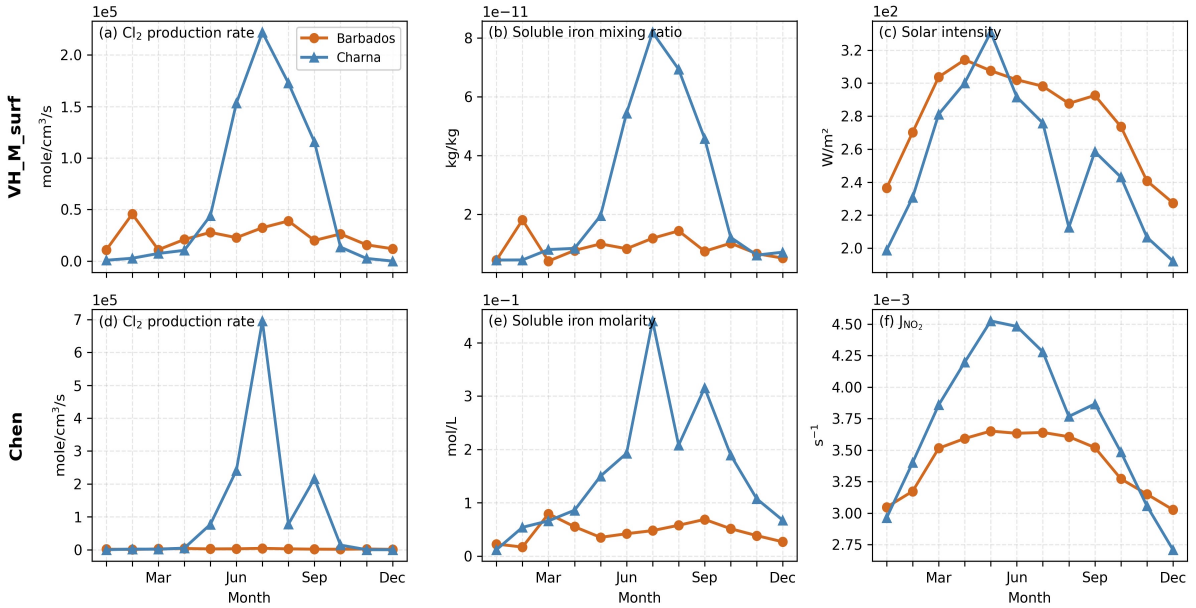
# Model simulations set-up

Resolution: f09 (~1$^{o}$)
Simulation period: 1994 – 1999 (first two year for spin-up)
Methane: Fixed lower boundary condition
Chemistry: trop_strat_mam4_slh  Emission: CMIP6

| Cases | MDSA scheme | Vertical limitation |
|---|---|---|
| **Current** | | |
| Ctrl | noMDSA | |
| VH_M_surf | VH_M scheme | Limited to 900hpa |
| Chen | Chen scheme | Effective for whole atmosphere |
| **Iron_x100** | | |
| VH_M_surf | VH_M scheme | Limited to 900hpa |
| Chen | Chen scheme | Effective for whole atmosphere |

# Iron-catalyzed $Cl_2$ production rate




- VH_M_surf scheme calculates higher Chlorine production rates over Atlantic, while Chen scheme simulates higher values over coastal regions (moisture decreases, molarity increases).
- Chlorine production rates are higher in summer
- Both scheme simulate higher rates in Charna than Barbados

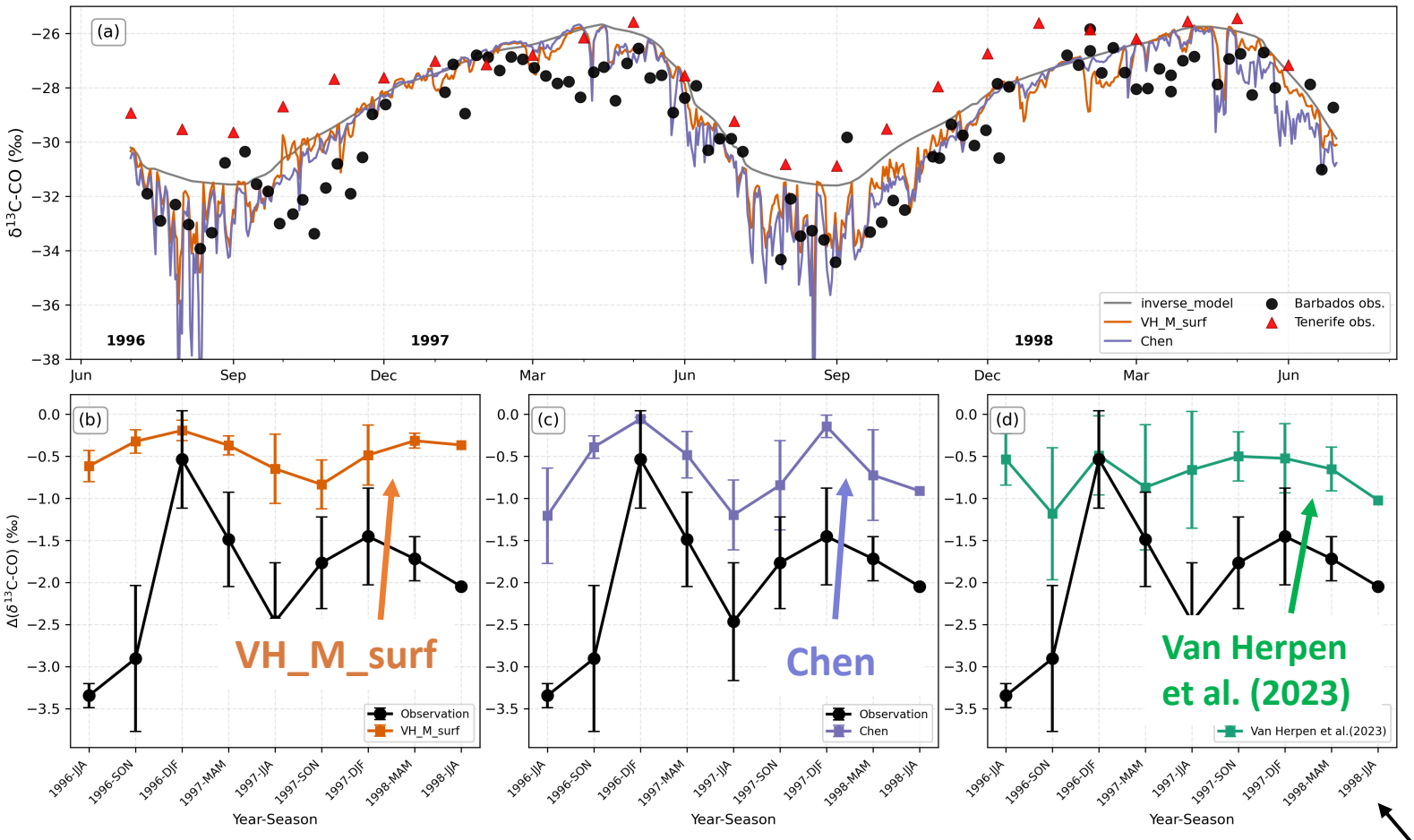
Barbados: Isotopic CO observations available

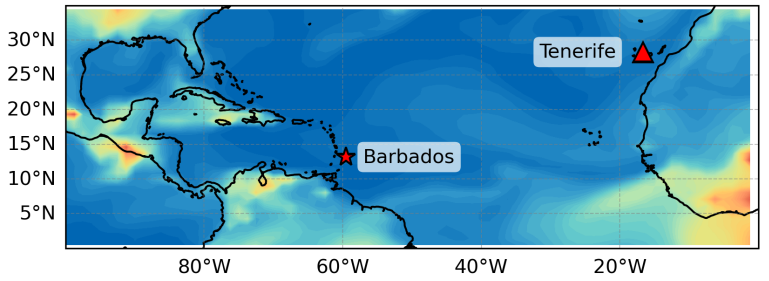
Charna: For High $Cl_2$ production rates analysis

# $^{13}$C-CO isotopic seasonal changes and shifts between the sites

13C-CO isotopic shifts

$$\delta^{13}\text{C-CO} = \frac{\Delta\text{CO}_{\text{CH}_4+\text{Cl}}}{\text{CO}_{\text{total}}}\left(\delta^{13}\text{C-CO}_{\text{CH}_4+\text{Cl}} - \delta^{13}\text{C-CO}_{\text{ambient}}\right) + \delta^{13}\text{C-CO(ref)}$$



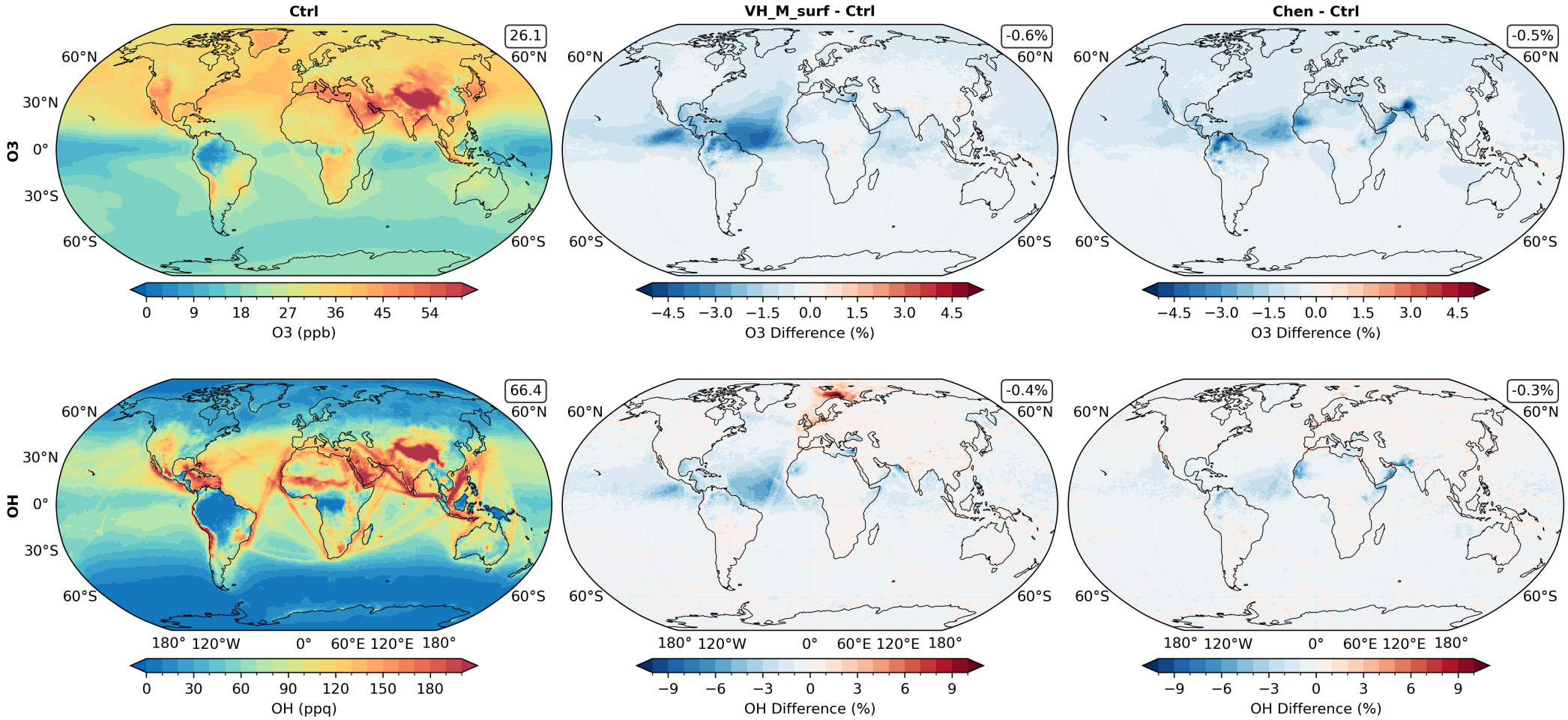




- All the schemes can capture the strong $^{13}$C-CO shift over Autumn seasons.
- Chen scheme shows better correlation to capture the shift between the sites.

13C-CO isotopic shifts between Barbados and Tenerife

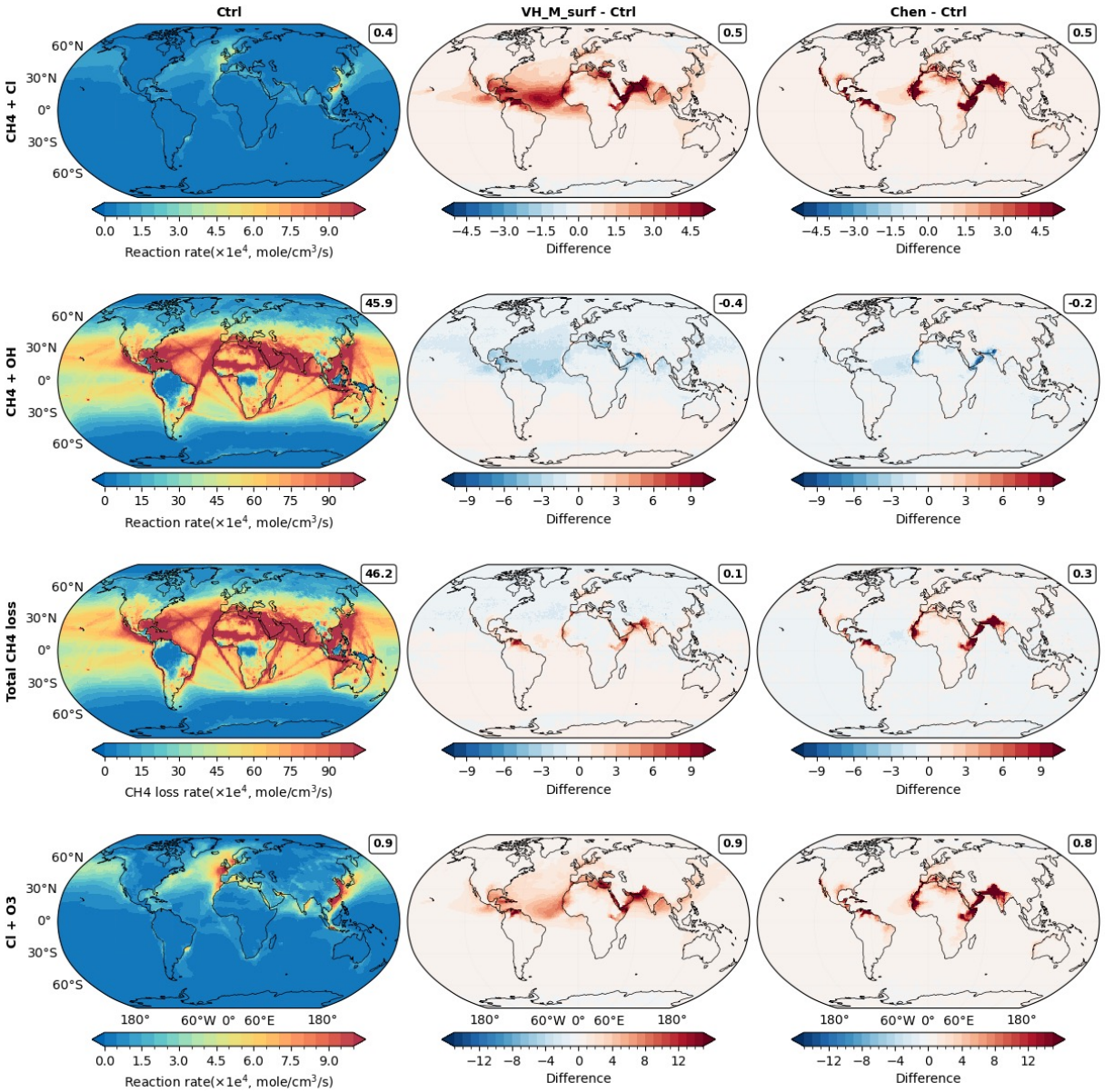
$$\Delta(\delta^{13}\text{C-CO}) = \delta^{13}\text{C-CO}_{\text{Barbados}} - \delta^{13}\text{C-CO}_{\text{Tenerife}}$$

# Effects on Ozone and OH distribution




- In both schemes, $O_3$ and OH changes are less than 1% globally.
- Both schemes simulate $O_3$ and OH depletion over North Atlantic region, but Chen scheme also sees efficient Iron reaction over coastal regions.

# Oxidation rates changes




**$CH_4$ + Cl** ↑

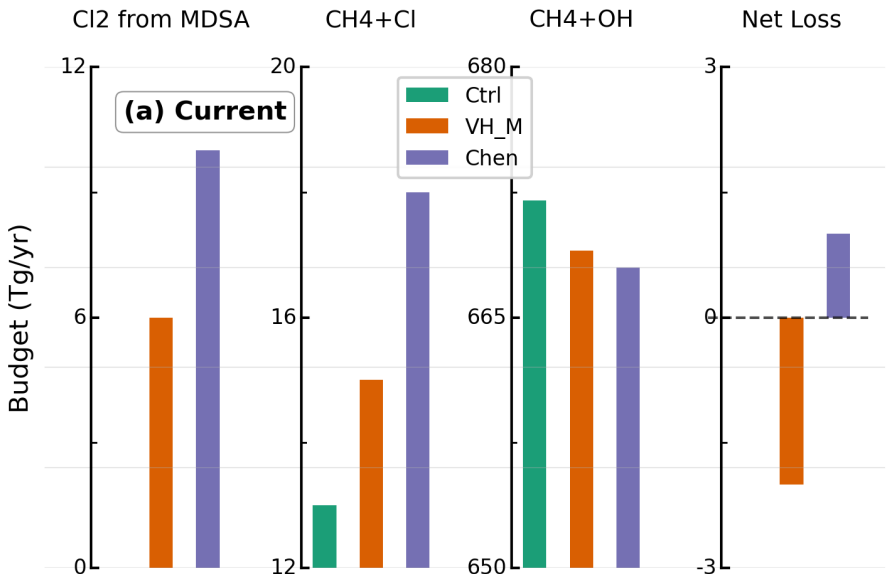
**$CH_4$ + OH** ↓

**Total $CH_4$ loss** ↑

**Cl + $O_3$** ↑

| Reaction (mole/cm3/s) | VH_M_surf | Chen |
|---|---|---|
| $CH_4$+Cl | +0.5 (+242%) | +0.5 (+718%) |
| $CH_4$+OH | -0.4 (-0.7%) | -0.2 (-0.9%) |
| Total $CH_4$ loss | +0.1 (+0.4%) | +0.7 (+0.3%) |
| O3+ Cl | +0.9 (+215%) | +0.8 (+585%) |

# Effects on Methane budget: Current



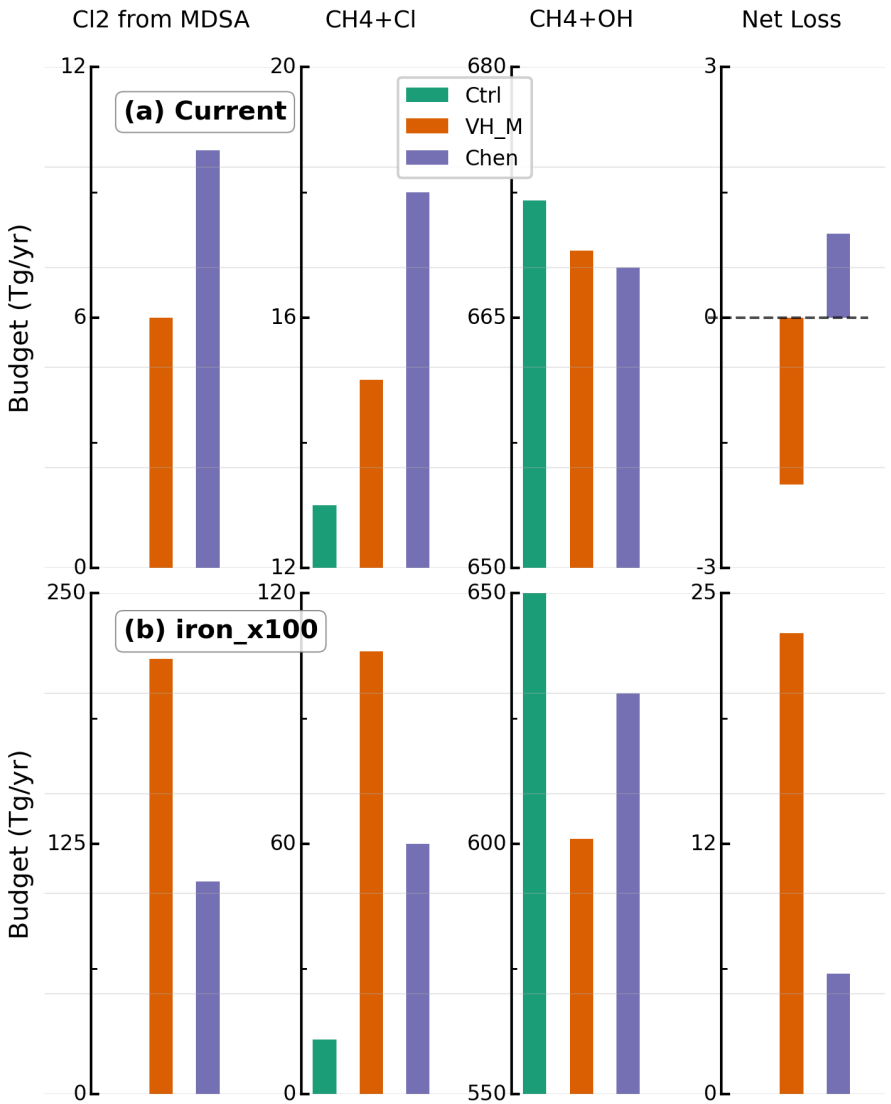

**Methane loss pathways:**

- ❑ $CH_4$ + Cl: +2 Tg/yr in VH_M and +5 Tg/yr in Chen
- ❑ $CH_4$ + OH: -3 Tg/yr in VH_M and -4 Tg/yr in Chen

**Net $CH_4$ loss:**

- ❑ -2 Tg/yr in VH_M
- ❑ +1 Tg/yr in Chen

# Effects on Methane budget: Iron_x100 (200 Tg/yr more iron)



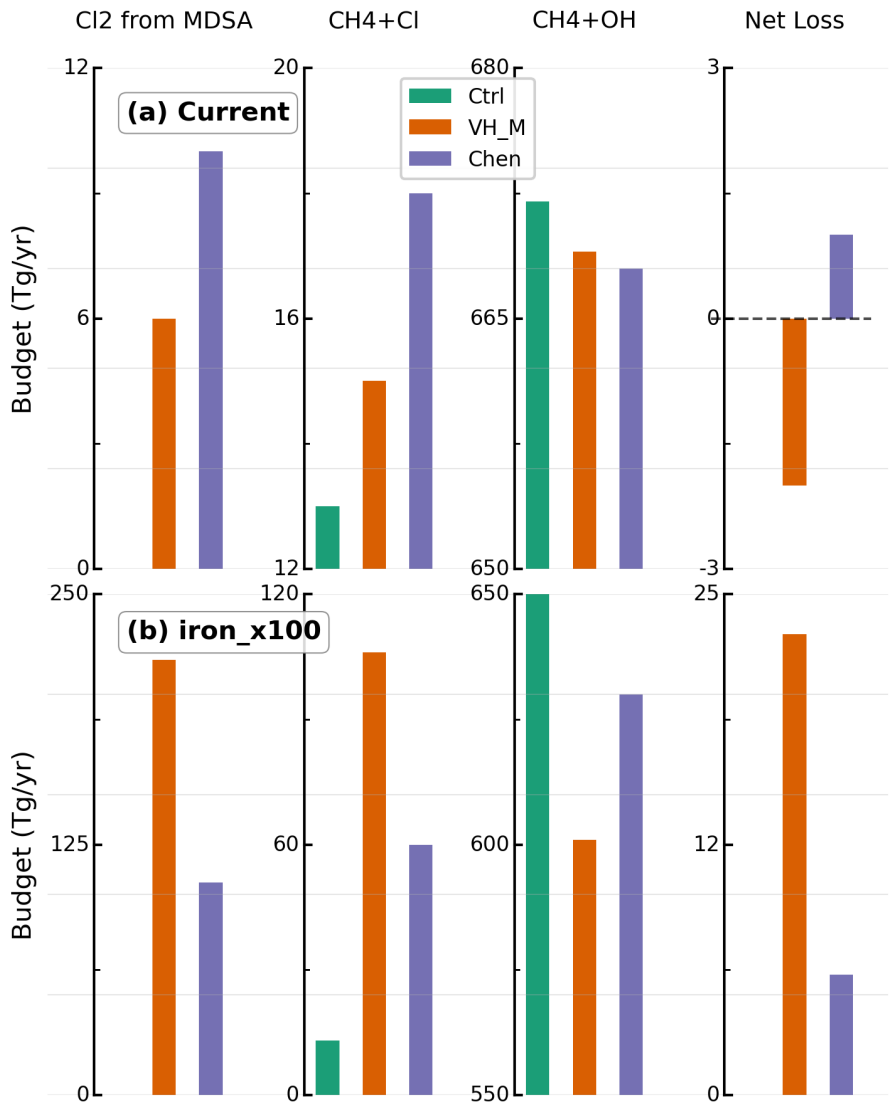

**Methane loss pathways:**

- ❑ $CH_4$ + Cl:  + 93 Tg/yr in VH_M and +47 Tg/yr in Chen
- ❑ $CH_4$ + OH: -71 Tg/yr in VH_M and -42 Tg/yr in Chen

**Net $CH_4$ loss:**

- ❑ +22 Tg/yr in VH_M
- ❑ +5 Tg/yr in Chen

# Effects on Methane budget: Iron_x100 (200 Tg/yr more iron)




## Takeaways

1. Two different schemes From Wittmer et al. (2015) implemented in CESM-SLH-MIMI-MDSA: VH_M_Surf and Chen

2. Similar results at Barbados and Tenerife (weak station shifts compared to observations)

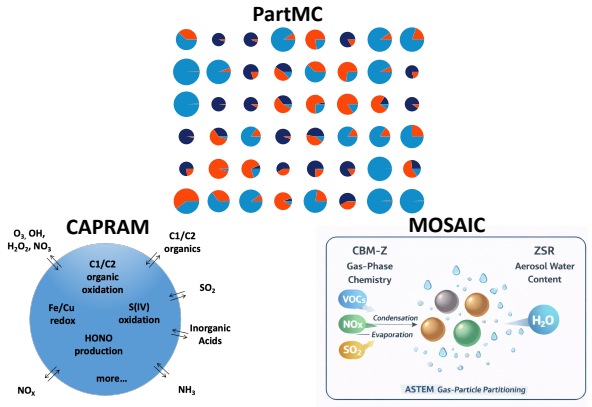
3. Methane modest response at Current environment (-2 Tg/yr in VH_M and +1 Tg/yr in Chen)

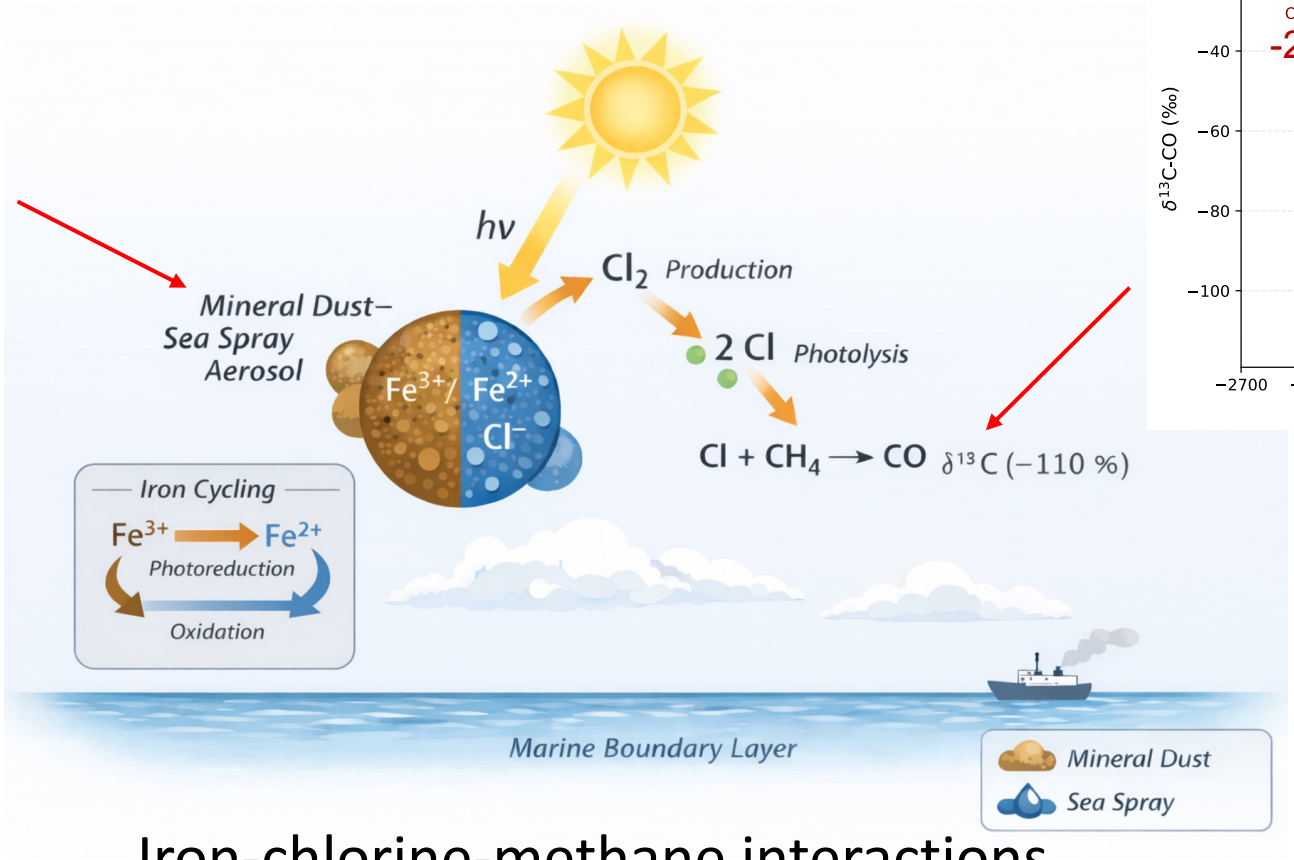
4. Methane loss increase 22 Tg/yr in VH_M and 5 Tg/yr in Chen in Iron_x100 (200 Tg iron added over the ocean)

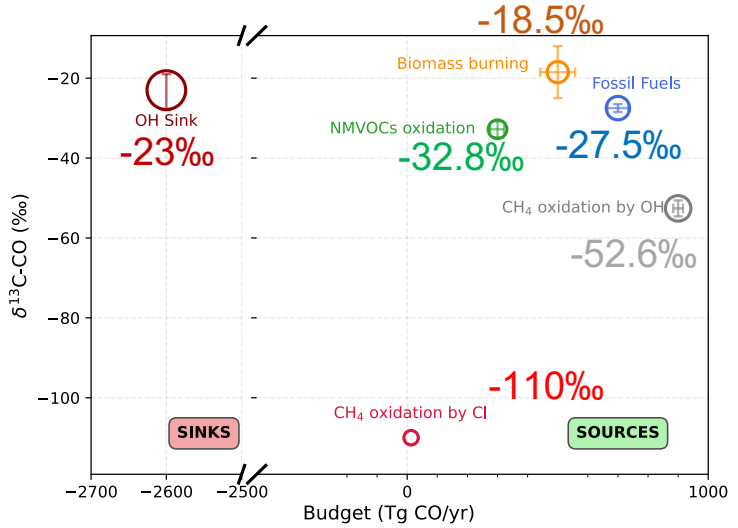
# Future works

**Future work 1:** Using particle-resolved box model and lab measurements to understand the chlorine production rate and constrain current parameterizations
(with Prof. John Mak, Prof. Alexander Laskin
Prof. Daniel Knopf and Prof. Cassandra Gaston)

**Future work 2:** Constrain CO budget and CO isotopic processes using CO tag model and field observations
(with Dr. Ben Gaubert and Prof. John Mak)



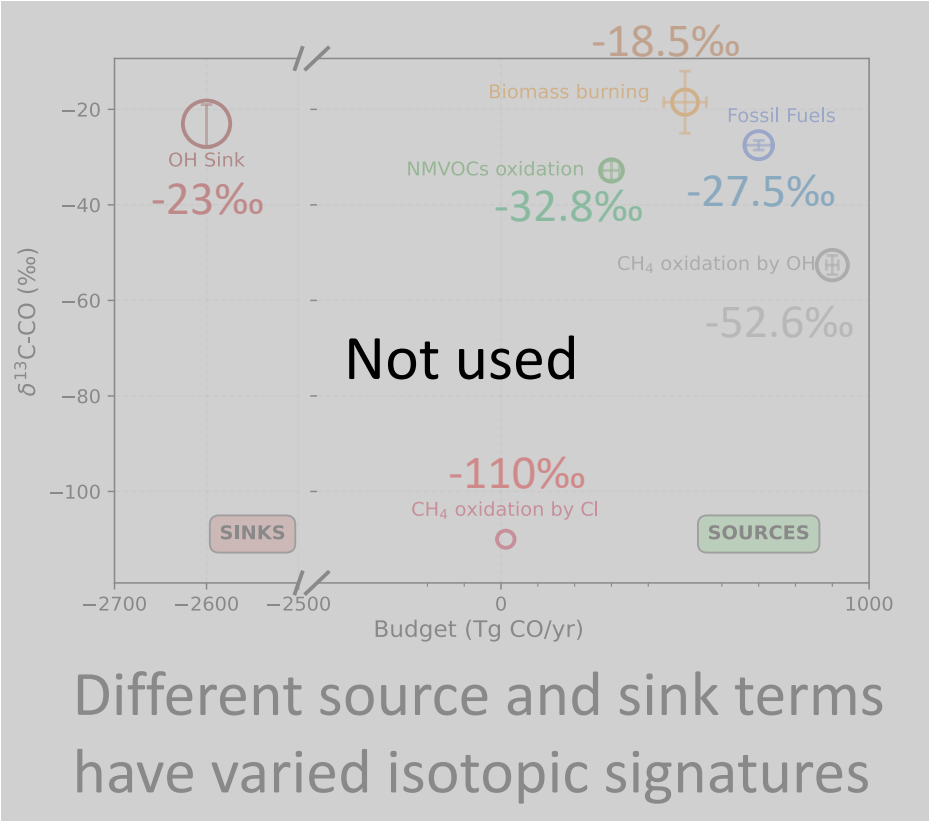




Iron-chlorine-methane interactions

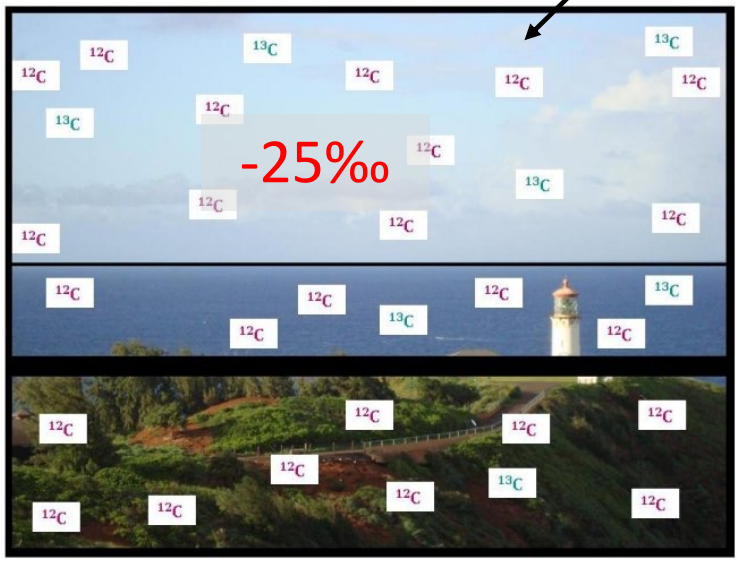
# Thank You. Questions?

# $^{13}$C-CO isotopic shift calculation



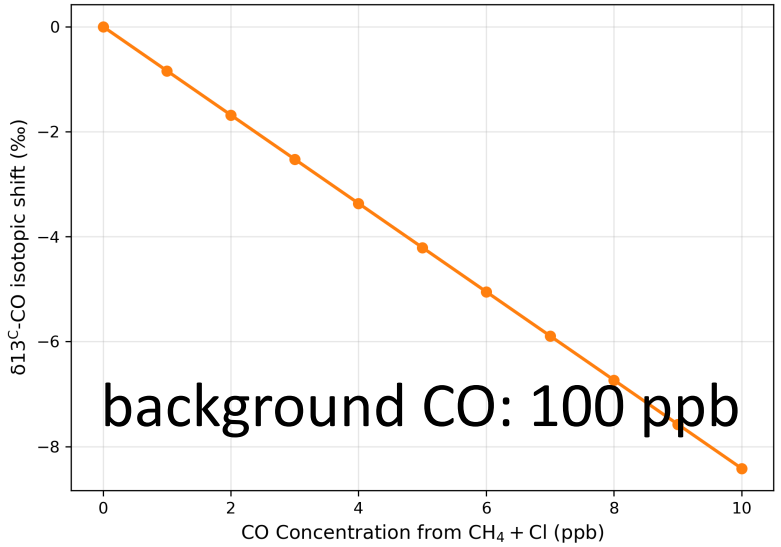

Different source and sink terms have varied isotopic signatures

$^{13}CH_4$ + Cl ----→ $\delta^{13}$C-CO (-110‰)



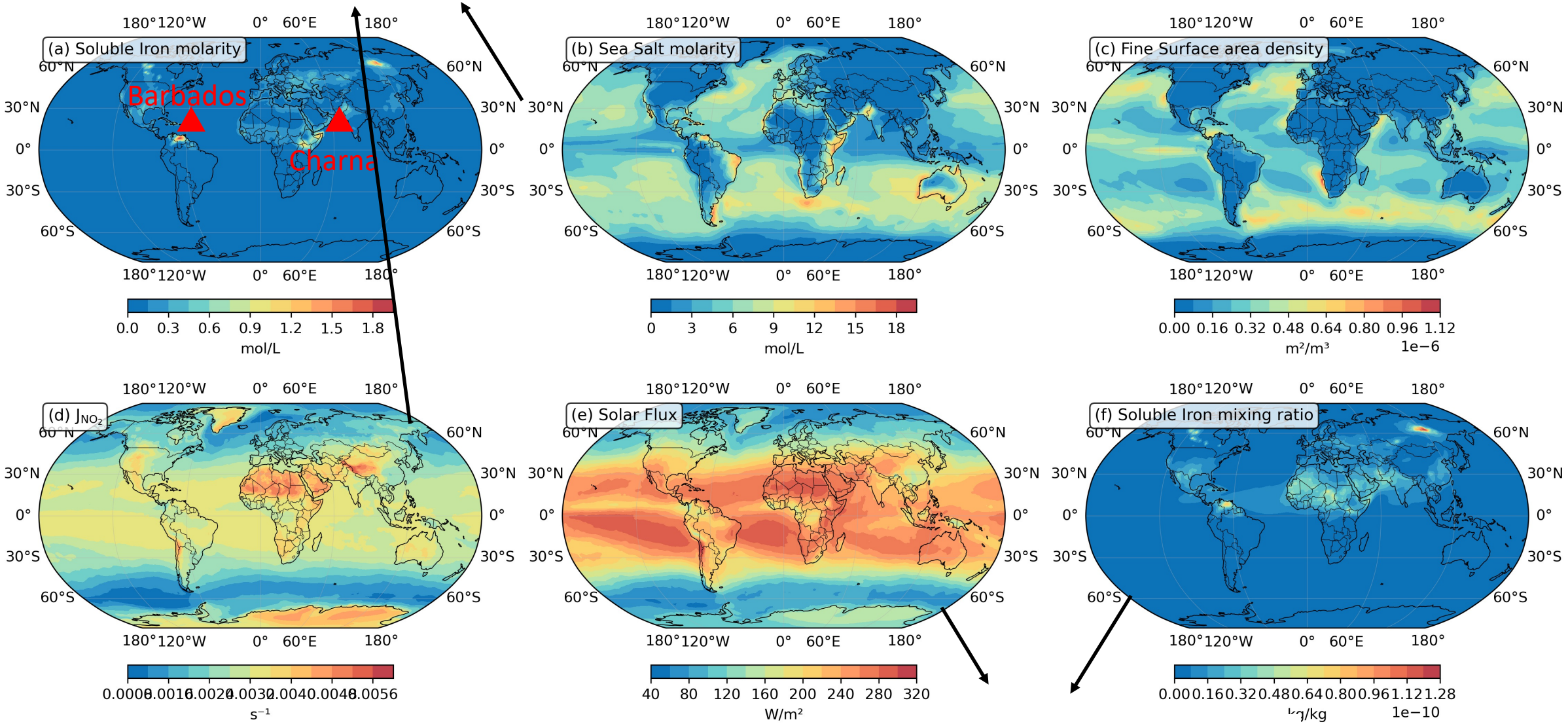

https://gml.noaa.gov/education/isotopes/stable.html

$$\delta^{13}\text{C-CO} = \frac{\Delta\text{CO}_{\text{CH}_4+\text{Cl}}}{\text{CO}_{\text{total}}}\left(\delta^{13}\text{C-CO}_{\text{CH}_4+\text{Cl}} - \delta^{13}\text{C-CO}_{\text{ambient}}\right)$$



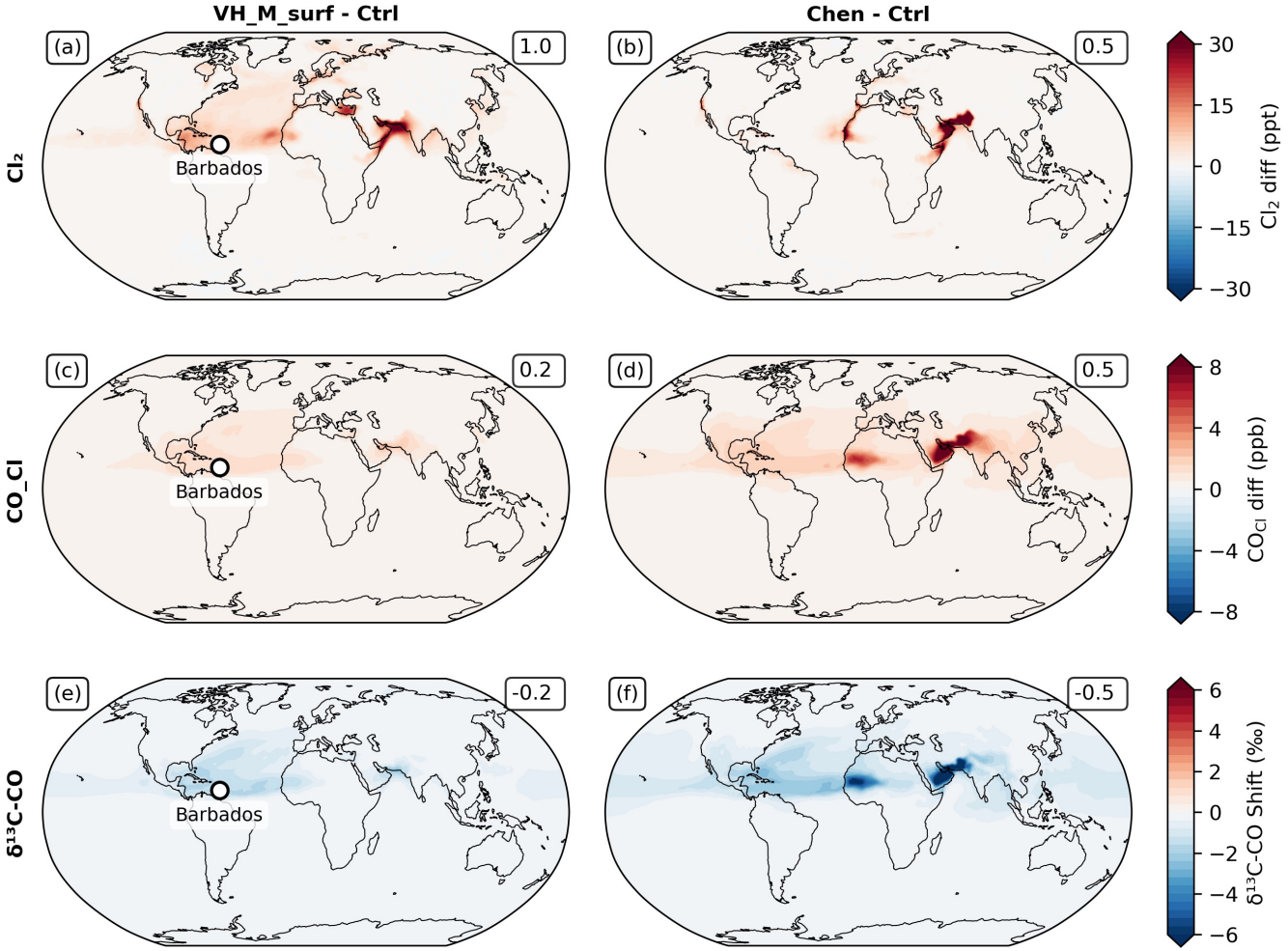
# Spatial distribution of reaction rate parameters

Chen: $\frac{d[Cl_2]}{dt} = \alpha_2[Fe_{sol}][Cl^-]j_{NO_2}S$




VH_M_surf: $\frac{d[Cl_2]}{dt} = \alpha_1 \chi_{Fe_{sol}} l$

# Why does less $Cl_2$ production over the North Atlantic result in similar $^{13}C$-CO shift in Chen scheme?




**Ctrl:** noMDSA

**VH_M_surf:** VH_M scheme for surface

**Chen:** Chen scheme for whole atmosphere

- ❑ More CO produced from $CH_4$ + Cl over coastal area in Chen scheme, transport to Barbados, even though the locally $Cl_2$ production rate is lower over Barbados.
- ❑ Longer lifetime of CO